SYNTHESIS OF PALM-BASED ZINC SOAPS FOR COMPOUNDING IN RUBBER PRODUCTS

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ABSTRACT

The melting point is the main factor in which metallic soap is to use as additives for the rubber manufacturing. This rubber compounder is the making stock for transfer moulding, compression, extruded profiles or hoses, the curing temperature or moulding and the duration will limit to the materials to be embedded on the surface of the compound. Zinc stearate has the lowest melting point as compared to other metallic soap. Although it has a low melting point, but it still consider high and problematic to the compounding system.

The main objective in this study is to synthesis a various zinc fatty acids soap to have a lower melting point that possess the same functions as zinc stearate. The zinc content of zinc fatty acids soap will be analysed by using MP-AES. The composition of the fatty acids will be analysed by Gas Chromatography. The iodine value is to determine the completion of the reaction. The melting point also will be recorded by using Mettler Tolendo FP 80.

The synthesised zinc fatty acids soap will be applied to the rubber compound to determine its performance ability.

ABSTRAK

Takat lebur adalah factor penting dalam penggunaan sabun logam sebagai bahan tambahan dalam penghasilan getah. Bahan tambahan ini berperanan dalam penghasilan acuan, pemampatan, pemulihan suhu atau acuan dan tempoh bahan tersebut melekat diatas permukaan campuran getah. Zink stearik mempunyai takat lebur paling rendah jika dibandingkan dengan sabun logam yang lain. Walaupun dengan takat lebur yang rendah, ianya masih lagi bermasalah dan dianggap tinggi di dalam sisyem penghasilan getah.

Objektif utama kajian ini adalah untuk menghasilkan sabun lemak asid zink yang mempunyai takat lebur yang lebih rendah tetapi berfungsi sama seperti zink stearik. Kandungan zink di dalam sabun ini akan dianalisis dengan menggunakan MP-AES. Komposisi lemak asid pula dianalisis dengan menggunakan Gas Chromatography. Kandungan iodin digunakan sebagai petunjuk samada reaksi lengkap telah berlaku. Takat lebur akan ditentukan menggunakan Mettler Toledo FP 80.

Sabun lemak asid zink yang dihasilkan dan digunakan di dalam campuran getah untuk menentukan prestasinya.

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NERVE	Polymer viscosity
SBR	Styrene butadiene
CPE	Chlorinated polyethylene
PE	Polyethelene
CR	Polychloroprene
DSC	Differential scanning calorimetry
TG	Thermogravimetric
LDL	Low density lipoprotein
MGs	Monoacylglycerols
DGs	Diacylglycerols
FFAs	Free fatty acid
KOH	Potassium hydroxide
$Na_2S_2O_3$	Sodium thiosulfate
KI	Potassium iodide
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
MSTFA	N-Methyl-N-(trimethylsilyl) trifluoroacetamide
GC-MS	Gas chromatography - mass spectroscopy
MP-AES	Microwave plasma - atomic emission spectroscopy
SFD	Spiral flow distance
TC	Curing time

CHAPTER ONE

INTRODUCTION

1.1 Processing Additives

Processing additives is any material that are used at relatively low dosage levels to improve processing characteristics of products without significantly affecting physical properties. The effect is improved the chemical or physical of the nature compounding products. The use of processing aids are to correct poor process ability that was frowned on by many compounders. In the modern of process aids are seen as process promoters to enhance the efficiency of rubber production processes.

The early mixtures of substances like well-defined antioxidants or accelerators usually lack uniformity in the compounding process. This will make the different to cross-linking reactions involving accelerators or the reaction of antioxidants. Many additives usually have multiple functions and their number has significantly increased over the years, for example to improve the flow, reduce tackiness, less mould fouling, mould cleaning, etc. Therefore, it is important to make a correct product selection and to well understand the role of each individual product available.

During mixing on the open mill or in internal mixer, the compounding materials should homogeneous blending of different polymers. It also enable quick incorporation of the compounding materials with filler. Excessive sticking to the machines or bagging must be avoided. Hence, the additives are added to facilitate homogenous blending and to reduce the tackiness of compound if possible. Compounding viscosity should be lowered. The uniform distribution and optimize dispersion of all compounding materials

is possible. The mild and energy efficient mixing at low temperature. Therefore, the mixing time could be reduced. Profile compounds should extrude fast, easily and uniformly. Thus products are needed for down line processing which function as lubricants or tackifiers and which control the rheological properties of the compound. In the vulcanization process, the compounding should have good flow properties in order the mold quickly, uniformly and free of trapped air which is particular on transfer or injection molding. Finally, the vulcanizates should not produce mold fouling residues. (Struktol, 2004).

Table 1.1: Problem of the rubber compounding. (Struktol, 2004).

Problem areas	**Operation**	**Benefits**
Mixing	Homogenization	Compatibility
	Polymer Viscosity (NERVE)	Viscosity Reduction
	Filler Incorporation	Mixing Time
		Dispersion
	Sticking	Release
Semi Products	Extrusion	Flow
	Calendering	Release
	Building	Tack
Vulcanization	Compression Molding	Flow
	Transfer Molding	Release
	Injection Molding	Less Mold Fouling
	Continuous Vulcanization	Mold Cleaning

1.2 Type of Processing Additives

Different of the substances have different regarding their effects, of major interest to the compounder. It is more meaningful to subdivide the products according to their effects which is shown in Table 1.2. Here it can be clearly seen which substance can be assigned to which effect. Several classes of substances exhibit multiple effects like metal soaps as improving flow ability, lubricities and also mold release function.

The stearic acid and zinc stearate were known as substances effectively improving the flow ability of rubber compounds. Calcium stearate is used as a parting and dusting agent. In the production of rubber for the pharmaceutical industry, it is often use processing additives in order to improve mold cavity fill, to improve dispersion or extrusion. The processing additives that have been used must not give off toxic, bactericide, bacteriostatic or haemolysis causing substances. They are substances which are toxicologically harmless, such as fatty acids, fatty alcohols, zinc or calcium soaps and fatty amides. Most of the processing additives used for pharmaceutical rubber products are from fatty acid derivatives.(Struktol, 2004).

The migration of solid or liquid compounding materials which have a limited solubility in the polymer matrix is usually happened in rubber compounding. It can be called as blooming effect. Very common, bloom refers to the initial formation of star-shaped clusters when solid compounding materials re-crystallize at the vulcanize surface. This is due to the fact that many of the rubber compounding materials have limited compatibility with the elastomer and separate out at the latest after vulcanizing and subsequent cooling to room temperature.(Ho, 2008).

Table 1.2: Effects of different processing additives to the compounder.(Struktol, 2004).

Effect	**Examples**
Peptization	2.2'- Dibenzamidodiphenyl disulfide
	Pentachlorothiophenol
	Zinc soaps
Dispersion	Fatty acids esters
	Metal soaps
Flow	Fatty alcohols
	Metal soaps
	Fatty acid esters
	Fatty aid amides
	Fatty acids
Homogenization	Resin blends
Tack	Hydrocarbon resins
	Phenolic resins
High hardness	High styrene resin-rubber
	Masterbatches
	Phenolic resins
Release	Trans-polyoctenamer
	Organosilicones
	Fatty acid esters
	Metal soaps
	Fatty acid amides

1.2.1 Metallic Stearate

Metallic stearate is a soap. They have widely used in industrial sector especially used as release coatings for uncured rubber. Typically, they are zinc, calcium and magnesium stearate. Zinc stearate is more common to use one to date. In general, the stearates are thought of as a salt. This salt is compound of metals with fatty acid derived from oil either is from animal or plant. The common acid used being stearic acid which contains of C18 chains. This salt, or soap of a stearic acid is formed by replacing the carboxylic hydrogen by a metal to yield a salt.(Hallstar, 2005).

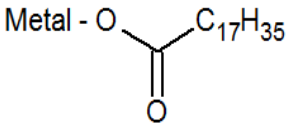


Figure 1.1: Carboxylic Hydrogen replaced

The combination of the metallic, zinc, calcium and magnesium would, therefore yield astearate formula as seen in

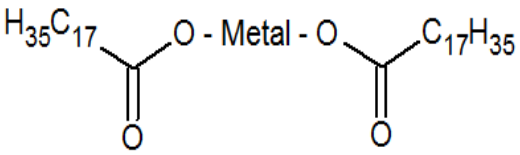


Figure 1.2: Chemical structure of metallic stearates

All three stearates have similar physical properties. The most difference between all three stearates as it relates to their melting points. The common stearates of their melting points are shown in Table 1.3. The melting point is a decide factor of which type of metallic soap to be used on the surface of the uncured rubber. When the rubber compounder is making stock for transfer molding, compression, extruded profiles or

hoses, the cure temperature or molding and time duration will limit to the materials on the surface of the compound. With the low melt point of zinc stearate, this has typically not been a problem. The zinc stearate will melt during molding and be absorbed into the compound without leaving discoloration or defects on the surface of the final molded rubber part.(Hallstar, 2005).

Table 1.3: Melting points of different metal stearates.(Hallstar, 2005).

Product	**Melting Point, ℃**
Zinc stearate	120
Magnesium stearate	140
Calcium stearate	160

The chemical structure of metallic stearates consists of a very long stable hydrocarbon chain. The long-chain hydrocarbon structure is insoluble in water and, thus, provides the hydrophobic nature of metallic stearates. The solubility parameter values of these stearates are low, and are similar to the common elastomers. Table 1.4 is shown the comparison solubility abilities of these stearates to elastomers. This data provides a better understanding on why metallic stearates have excellent compatibility in most elastomers. (Hallstar, 2005).

Table 1.4: Solubility of different processing additives.(Hallstar, 2005).

Stearates	**Solubility d [MPa/ (½)]**
Zinc Stearate	18
Magnesium Stearate	
Calcium Stearate	
Elastomer	16 - 20
Natural Rubber	
SBR	
Polyisoprene	
Polybutadiene 16 - 20	
CPE	
Acrylic	
Chlorosulfonated PE	
CR	

1.2.1.1 Calcium Stearates

Calcium stearates, which are recognized as physiologically safe, have become increasingly important in the last few years. They are insoluble in most solvents. They dissolve only slightly when heated in aromatic compounds, chlorinated hydrocarbons or vegetable and mineral oils and waxes. Calcium stearates are mainly used as lubricants, mould release agents and acid scavengers in the plastics industry. The pharmaceutical and cosmetic industries use calcium stearate as an anti-caking additive for powder and granules and as an excipient for pressing tablets. The building industry uses it as hydrophobic agent for inhibiting moisture absorption and preservation of building materials and construction.(Baerlocher, 2005).

Calcium stearate shows some interesting effects when heated. It dehydrates and starts to soften at temperatures between 120 and 130 ℃ and takes a viscous consistency at approx. 160 ℃. This state lasts whilst the material is heated occurring some slight discoloration. The thermogravimetric diagram (TG) shows that calcium stearate loses about 3 % of its weight at approx. 100 ℃. This weight loss corresponds to one mole water of crystallization, which is split off at this temperature. A differential scanning calorimetric-measurement (DSC) indicates this separation of water crystallization by an endothermic peak. The temperature-dependent X-ray diffraction diagram demonstrates that the crystalline structure of calcium stearate changes as a consequence of the separation of water crystallization.(Baerlocher, 2005).

1.2.1.2 Zinc Stearates

Zinc stearates are insoluble in polar solvents, but more soluble in aromatic compounds and chlorinated hydrocarbons when heated. Their main application areas are the plastics and rubber industries where they are used as release agents and lubricants which can be easily incorporated. The outstanding clarity and heat stability properties of crystal clear zinc stearate grades make them particularly suitable for impact and crystal grade polystyrene and other clear polymers. Zinc stearate functions as an acid scavenger and processing aid in certain polyolefin applications.(Baerlocher, 2005).

The paint and coatings industry uses zinc stearates for pigment suspension and to improve grind ability and matting. The building industry uses powdered, precipitated zinc stearates as hydrophobic agents for plasters.(Baerlocher, 2005).

Zinc stearate can only be observed when the vulcanizate is slowly cooled and diffusion to the rubber surface can take place. Nevertheless, amines as accelerator decomposition products will complex and solubilize the zinc, thus zinc stearate does not appear at the vulcanizate surface. But when in contact with water vapor, insoluble basic zinc stearate can be formed and bloom out.(Ho, 2008).

1.2.1.3 Magnesium stearates

The magnesium stearates almost insoluble in normal solvents. They are able to hold considerable quantities of water and take on a creamy consistency. Magnesium stearates are therefore used to improve the retention of creams and semi-rigid wax articles as well as to produce waxes. Since they are recognized as physiologically safe, they are used by the cosmetics and pharmaceutical industry.(Baerlocher, 2005).

Magnesium stearates improve the free-flowing properties and are added as anti-caking agents to powders. One of the principle uses of magnesium stearate is as a tablet excipient in pharmaceutical dosage forms. Thermo stable magnesium stearates are used as lubricants and release agents for the processing of thermoplastics and thermosets. (Baerlocher, 2005).

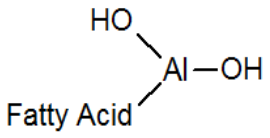
1.2.1.4 Aluminium Stearate

Aluminium stearates are produced by the precipitation process only. There are three possible combinations of aluminium with fatty acids: The ratio of aluminium to fatty

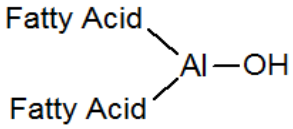
acid does not necessarily correspond to the stoichiometric values. Any ratio is possible between the extremes 1:1 and 1:3. Therefore there are many varieties of aluminium stearates, generically referred to as aluminium mono-, di- or tri-stearate, whose properties differ from one another in respect to physical properties such as melting point, free fatty acid and particularly the gelling properties. Oils with a low viscosity are best thickened by aluminium tri- and di-stearates, whilst very viscous oils form stiffer gel when combined with aluminium di- or mono-stearates.(Baerlocher, 2005).

The melting point of aluminium greases usually range from 110 to 120 ℃. Special stearates whose dropping point exceed 200 ℃. All aluminium greases are highly hydrophobic and are characterised by outstanding transparency and good adhesion to metallic surfaces. Due to their excellent water repellency, aluminium stearates are used in coatings and building industry materials as water repellent ingredients.(Baerlocher, 2005).

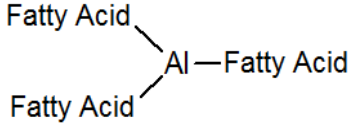
Aluminium mono-, di- and tri-stearates are insoluble in water, lower alcohols, esters and ketones. In benzenes, aromatic compounds and halogenated hydrocarbons as well as in natural and mineral oils, they dissolve to a gel when heated.



Aluminium Mono Stearates



Aluminium di-stearates



Aluminium tri-stearates

1.2.1.5 Alkali Stearates

1.2.1.5.1 Lithium Stearates

Hydrophilic lithium stearates distinguish themselves by their excellent swelling properties. Different compositions of fatty acids are available in the product range. Depending on the product type properties like melting point temperatures of greases containing lithium stearates are much higher than those of aluminium stearates. Lithium stearates are widely used to thicken natural as well as synthetic oils and help to increase the melting point and flexibility of micro-crystalline waxes and paraffins. They are also used during the production of light weight metal mouldings. The advantage of lithium stearates with long fatty acid chain lengths is the minimal residue after thermal treatment.(Baerlocher, 2005).

1.2.1.6.1 Sodium Stearates and Sodium Oleates

Sodium stearates and oleates are produced by direct reaction according to a patented process. Possible applications of these products are e.g. swelling of alcohols, lubrication and nucleating during the processing of thermoplastics.(Baerlocher, 2005).

Sodium oleates are mainly used as hydrophobic agents for building plasters, where homogenous dispersion is easily obtained due to its solubility in water. The alkaline components of the plaster and the sodium stearate forms a calcium stearate which is also finely dispersed, thus imparting high water-repellency properties to the plaster.(Baerlocher, 2005).

1.1 Objectives

The melting point is the main factor of which metallic soaps to be used on the rubber manufacturing. The rubber compounder is the making stock for transfer moulding, compression, extruded profiles or hoses, the cure temperature or moulding and time duration that will limit to the materials on the surface of the compound. Zinc stearate is the lowest of melting point compare with other metallic soap. Although it has a low melting point, but it still consider high and problematic to the compounding system frequently.

In this study, the main objective is to synthesis zinc fatty acids soap containing unsaturated fatty acids that have a lower melting point to reduce the blooming effect on the compounder. Zinc soaps of branched or aromatic carboxylic acids are soluble in rubber. They can provide substantial improvement in creep and modulus reproducibility as compared to zinc stearate.

The synthesised compounds will utilized in rubber compounding and its performance ability will be evaluated.

CHAPTER TWO

LITERATURE REVIEW

2.1 Materials

Currently about 117 million tonnes per annum of oils and fats come from vegetable and animal sources. There were 17 commodity oils production in world and only out of four are of animal origin.(Oil World Publications, 2002). Of the total production of oils and fats, about 80% is used for food purposes, 6% is used in animal feed, and the remaining 14% provides the basic of the oleochemical industry.(Gunstone and Hamilton, 2001).

Table 2.1 shows the annual average production of 17 oils and fats for selected five year periods from 1976/80 with forecasts up to 2016/ 20 taken from a revised Oil World publication in 2002. That is a period of forty years. There has been a considerable increase in oil and fat production during that time from 53 million tonnes in 1976/80 to 105 million in 1996/2000 with 185 million tonnes expected in 20 years' time.(Frank D. Gunstone, 2006)

The production levels of all the oils have increased during the past 20 years and further increases are expected in the coming years. However they have not all increased simultaneously. They still have some oils lost the market share. Palm oil and soybean oil have increased considerably to take up the front of positions in the order of production level. But, it is considered that palm oil production will exceed that of soybean oil towards the end of the twenty years period.(Frank D. Gunstone, 2006).

The production palm oil is expected increases dramatically in future time. A study by a group of researchers from the Institute of Nutrition and Food Hygiene, Beijing, China compared the effects of palm oil, soybean oil, peanut oil and lard. The palm oil has the effect of decreasing total blood cholesterol and 'bad' LDL-cholesterol and increasing the level of 'good' HDL-cholesterol. They showed that palm oil, Soya bean oil and peanut oil had no effect on the blood cholesterol but lard increased the cholesterol levels. Palm oil has the lowest cholesterol level among these hyper cholesterolemic subjects. (Zhang et al., 1997a; Zhang et al., 1997b; Zhang et al., 1995).

Table 2.1: Annual average production of 17 oils and fats in selected five-year periods from 1976/80 with forecasts up to 2016/20.(Mielke,2002)

	1976/80	1986/90	1996/00	2006/10	2016/20
World total	52.65	75.66	105.06	165.65	184.77
Soybean oil	11.23	15.28	23.14	33.60	41.12
Cottonseed oil	2.83	3.64	4.00	5.35	6.51
Groundnut oil	3.01	3.70	4.55	5.72	6.38
Sunflowerseed oil	4.21	7.25	9.11	12.43	16.97
Rapeseed oil	3.01	7.51	12.64	17.72	22.69
Sesameseed oil	0.51	0.64	0.70	0.86	0.96
Corn oil	0.83	1.35	1.92	2.49	3.16
Olive oil	1.68	1.80	2.47	2.75	2.98
Palm oil	3.69	9.22	18.72	31.43	43.36
Palmkernel oil	0.46	1.21	2.34	3.84	5.28
Coconut oil	2.85	3.07	3.01	3.70	4.55
Butter	5.60	5.60	5.81	6.93	7.99
Lard	4.25	4.25	6.38	7.93	9.14
Fish oil	1.13	1.13	1.25	1.18	11.59
Linseed oil	0.79	0.79	0.70	0.81	0.97
Castorseed oil	0.32	0.32	0.46	0.71	0.78
Tallow	6.24	6.24	7.85	10.06	10.76

2.1.1 Palm Oil

The oil palm tree *(Elaeis guineensis jacq.)* originates from West Africa where it grows in the wild. It was introduced and developed by the British in early 1870's as an ornamental plant. The Tennamaran Estate in Selangor as the foundations for the oil plantations and palm oil industry in Malaysia.(http://www.mpoc.org.my/, 2014)

Today, 4.49 million hectares of land in Malaysia is under oil palm cultivation; producing 17.73 milliom tonnes of palm oil and 2.13 tonnes of palm kernel oil. Malaysia is the one the largest producers and exporters of palm oil in the world, accounting for 11% of the world's oils and fats production and 27% of export trade of oils and fats.(http://www.mpoc.org.my/, 2014)

Most of the palm oils are used in food application and nearly up to 90%. At present only 10% is used in non-food products. There can be categories to few groups in food application. Among the commonly used vegetable oils and fats, palm oil is by far the most versatile. After refining, palm oil possesses all the characteristics required for many uses without hydrogenation. By fractionating palm oil, its uses are further increased.(http://www.mpoc.org.my/, 2014)

More palm oil is used for frying and cooking than for any other purposes. Palm oil in combination with hydrogenated palm oil can be used to produce shortenings of excellent quality and diverse applications, such as for making cakes, bread, cream, pastries and sweets. Margarine is a water in-oil emulsion similar to butter in texture and appearance. Other uses of palm oil include spray oil, filled milk, ice cream powder and cream fillings. The most important is filled milk which most of the butter has been

replaced by vegetable oil. The product has better keeping quality than natural milk while being similar taste.

Besides the food application, palm oil still used in non-food products and mainly as an ingredient for making soap and oleochemicals. Oleochemicals are chemicals derived from oils and fats. They are analogous to petrochemicals which are chemicals derived from petroleum. The hydrolysis or alcoholysis of oils or fats is the basis of the oleochemicals industry. The hydrolysis of the triglycerides composing oils and fats produces various fatty acids and glycerol, whereas alcoholysis gives fatty acid esters and glycerol. Fatty acids or their esters can be used as the starting materials for making fatty alcohols and fatty nitrogen compounds. These products can be further modified to produce various derivatives. Hence oleochemicals are often divided into at least two categories, which are basic oleochemicals and their derivatives. The five basic olechemicals are fatty acids, esters, alcohols, nitrogen compounds and glycerol (Figure 2.1).(Ong et al, 1990).

2.1.2 Methyl Esters

Methyl esters were prepared from mixed crude palm oil containing a high free fatty acid content by using a two-stage process. First stage, it was go through the esterification process and sulfuric acid was used as the catalyst. Then, it followed by a trans-esterification reaction and sodium hydroxide as the catalyst. Methyl esters are mainly used for the production of fatty alcohols and derivatives and sulphonated methyl esters. These products are then used in various applications such as detergents, cosmetics, lubricants, plasticizers and pharmaceutical products. Methyl esters can also be used as a diesel substitute.

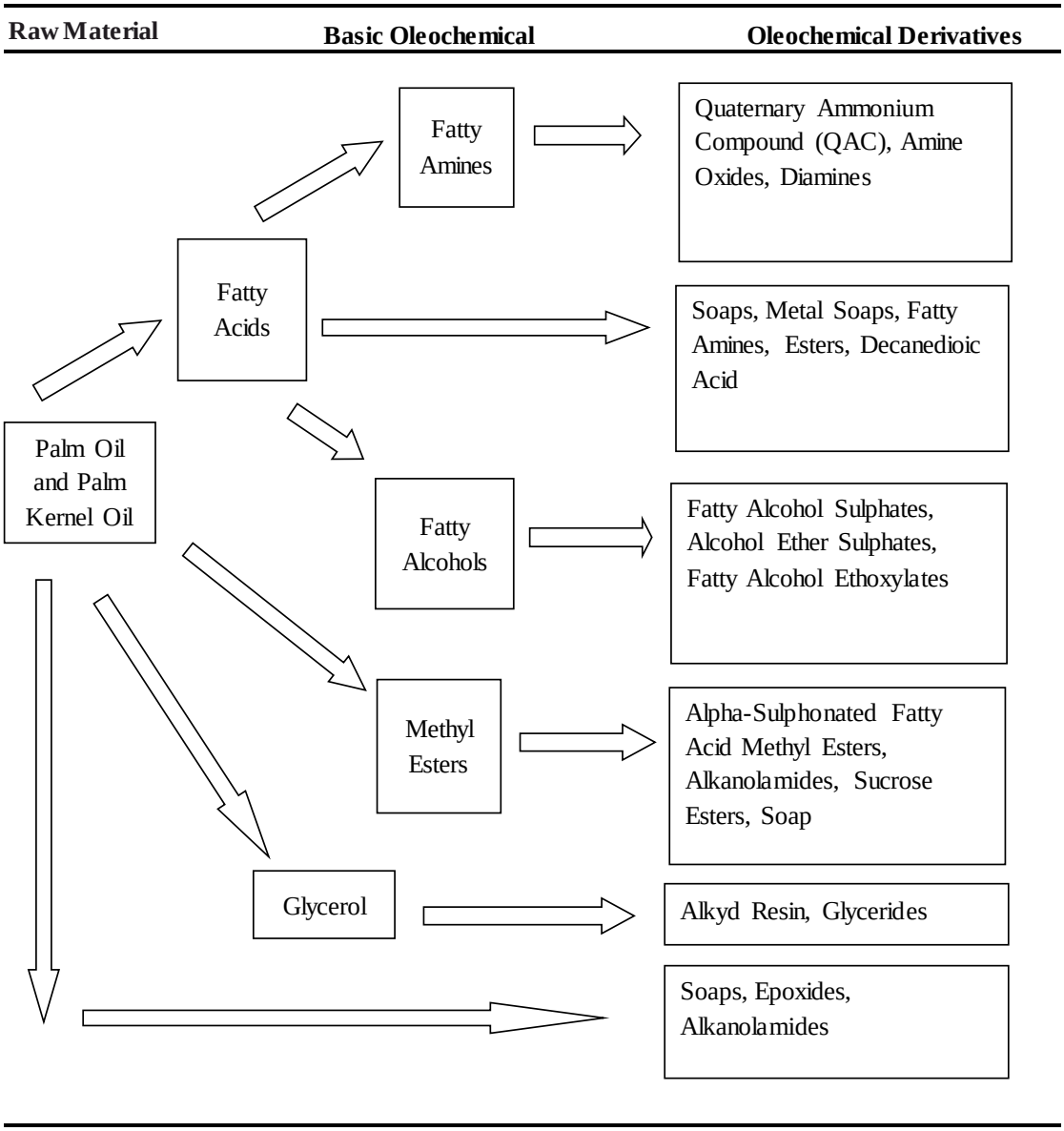


Figure 2.1: Oleochemical derivatives process. (Source:Choo, 2001)

2.1.3 Glycerol

Palm and Lauric oil are the major sources of natural glycerol. It is a by-product of fat splitting and it finds wide applications in pharmaceuticals, toiletries, industrial explosives, and as alkyd resins in the paint industry.

2.1.4 Fatty Acids

Fatty acids can be synthesis directly from palm oil and palm kernel oil through the saponification, alcoholysis or fat splitting. Saponification is a process that produces soap, usually from fats and lye. Soap is liberated by saponification and is further treated with acid to give free fatty acids. Splitting of oils and fats by hydrolysis of triglycerides to form free fatty acids and glycerol under basic conditions. The split- off fatty acids are a mixture ranging from C4 to C18 and depend on the type of oils and fats. In alcoholysis, fatty esters produced are treated with mineral acid to convert them to free fatty acids.

Most of the fatty acids are present as trigecerides. The different placement of fatty acids and fatty acid types on the glycerol molecule produces a number of different TGs. There are 7 to 10% of saturated TGs, predominantly tripalmitin.(Kifli. H, 1981). TGs are the major constituents of palm oil and it is consists of mixtures of TGs and glycerol molecules. Each TG will esterified with three fatty acids. The hydrophobic TGs attach to the fat or oil soluble cellular components during oil extraction. These are the minor components of palm oil such as phosphatides, tocopherols, pigments, sterols tocotrienols and trace metals. Other components are metabolites in the biosynthesis of TGs such as monoacylglycerols (MGs), diacylgycerols (DGs) and free fatty acids (FFAs).

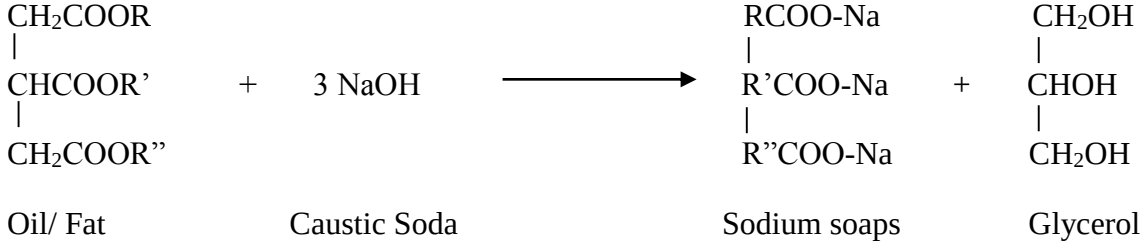
The fatty acids are any class of aliphatic acids, such as palmitic (16:0), stearic (18:0) and oleic (18:1) in animal and vegetable fats and oils. The major fatty acids in palm oil are myristic (14:0), palmitic, stearic, oleic and linoleic (18:2) (Siew, 2000). Table 2.2 shows the fatty acid composition of palm oil and palm kernel oil.

Table 2.2: Different type of fatty acids base on the number of carbons.(Source:Choo, 2001)

Fatty Acids	Carbon Number: Unsaturated Bond	Palm Oil	Palm Kernel Oil
Caproic	6:0	-	0.1-0.5
Caprylic	8:0	-	3.4-5.9
Capric	10:0	-	3.3-4.4
Lauric	12:0	0.1-1.0	46.3-51.1
Myristic	14:0	0.9-1.5	14.3-16.8
Palmitic	16:0	41.8-46.8	6.5-8.9
Palmitoleic	16:1	0.1-0.3	-
Stearic	18:0	4.2-5.1	1.6-2.6
Oleic	18:1	37.3-40.8	13.2-16.4
Linoleic	18:2	9.1-11.0	2.2-3.4
Others	-	0-1	Traces-0.9

2.1.5 Soap

Soaps are mixture of different valences of metal salts and long chain fatty acid. The most important metal soaps are based on calcium, zinc, magnesium and aluminium in term of quantity. The main advantage is their wide range of properties and can be applied in different field.



The use of soap as improver gelation and also can have a stabilizing effect whilst they can act as foam inhibition agent or acid scavenger. Although now detergents have almost eliminated the use of soap for home laundry purposes, but they still the main ingredient in toilet bars for personal use. They are used as lubricant, release agent or as water repellent. Metal Soaps are available in different product forms such as fine powders, flakes, pastilles and granules.

2.2 Methods of production of zinc stearate

There were four different methods for the production of zinc stearate, with each method imparting its own specific properties to the final product:

2.2.1 Precipitation (or double-decomposition) reaction

The fatty acid is saponified in large volume of heated water with an equivalent molar to a slight excess quantity of a strong alkali solution (caustic potassium solution, sodium hydroxide, ammonia). The alkali stearate is soluble in water (Figure 2.2). Particle morphology, surface area and particle size or shape are influenced by the precipitation rates and concentration of reactants. Basically, the higher the dilution of the saponified fatty acid, the larger the surface and the smaller the particles will be. The density is determined by these properties, which is typically low for precipitated metallic stearates. The desired water-insoluble metallic stearate is produced by adding a metal salt solution (e.g. aluminium sulphate solution, calcium chloride solution). The reaction follows the formula (Figure 2.3).(Baerlocher, 2005).

Sodium sulphate or sodium chloride is a water soluble salt, is generated as by-products of the precipitation reaction, must be removed from the metallic stearate by filtration and washing. Finally, the product must be dried and the product milled or de-agglomerated. This double-decomposition reaction typically produces fine and very light powders with a large surface area, and a more platelet morphology. These types of metallic stearates are used in applications requiring fine particle size and high surface area for the best lubrication and release properties and where special emphasis is placed on good hydrophobic properties.(Baerlocher, 2005).

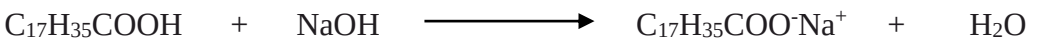


Figure 2.2: Reaction of stearic acid with sodium hydroxide (Baerlocher, 2005).

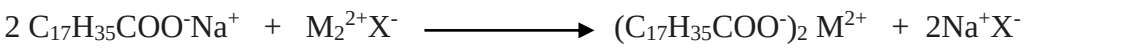


Figure 2.3: Reaction of sodium stearate with metal salt solution (Baerlocher, 2005).

M = Zn^{2+}, Ca^{2+} or similar ; X = Cl^- , ½ SO_4^{2-} or similar (Baerlocher, 2005).

2.2.2 Direct reaction

The reaction between stearic acid and hydroxide metal oxide, or carbonate takes place at an elevated temperature and with large excess of water. The reaction is shown that there are no by-products (Figure 2.4). Particle size, and thus bulk weight and particle surface are influenced by the relation of stearic acid to water. The higher the dilution, the smaller the particles and the larger the surface will be.(Baerlocher, 2005).

The metallic stearates produced by direct reaction has relatively fine powders with free of water-soluble salts and a high degree of purity. But, not all metallic stearates can be produced effectively by this method. These is because of the low reactivity of certain metal oxides carbonates or hydroxides.(Baerlocher, 2005).

The reaction can be run effectively at atmospheric pressure, but an advantage of this method is that it can also be run under pressure and at higher temperatures (>100 ℃) to produce certain types of metallic stearates, which cannot normally be obtained under atmospheric conditions by the direct reaction process. In most cases, the product must be filtered and dried to the final desired moisture content. Direct reaction in water generally produces a more rounded, agglomerated particle, with higher bulk density than precipitated stearates.(Baerlocher, 2005).

Figure 2.4: Reaction of steric acid with calcium hydroxide (Baerlocher, 2005).

2.2.3 Fusion process

During the fusion process, stearic acid and metal oxides or hydroxides are heated under pressure with continual stirring beyond the melting point of the metallic stearate product. As the melting point of most metallic stearates is higher than 100 ℃, the water resulting from the reaction escapes as steam. Therefore, a drying step is unnecessary. A variety of physical forms can be produced from this process, depending on the melting range of the final product. For relatively sharp or low melting metallic stearates, all forms (prills, pastilles, powder and flakes) are generally feasible. A very high degree of purity is achievable with the fusion process (Figure 2.5).

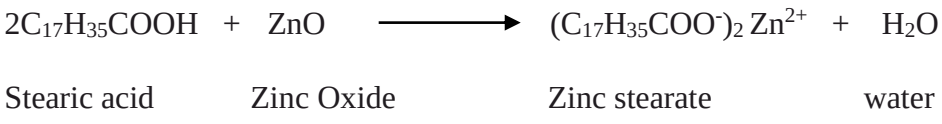


Figure 2.5: Reaction of stearic acid with zinc oxide (Baerlocher, 2005).

2.2.4 AV process

AV process is a combination of the fusion processes and direct reaction. Metal hydroxides or oxide are heated according to a patented method with a fatty acid and a small quantity of water in a pressurised reactor, with the final temperature corresponding more or less to the melting point of the soap. The added water and the water resulting from the reaction are removed under reduced pressure at the end of the reaction cycle. (Baerlocher, 2005).

The AV process allows the very efficient production of a variety of stoichiometry, including very pure products. AV technology is generally used to produce metallic stearates in free-flowing granule or powder forms (Figure 2.6). (Baerlocher, 2005).

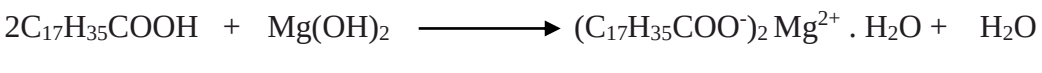


Figure 2.6: Reaction of stearic acid with magnesium hydroxide (Baerlocher, 2005).

CHAPTER THREE

METHODOLOGY

3.1 Procedure of zinc soaps containing unsaturated fatty acids by fusion process

Zinc soap were obtained by fusion process which it is consider as simple process and can produce high yield of product. Firstly, prepare a mixture of saturated and unsaturated fatty acids with the ratios of stearic acid to palm kernel: 1:2.

Zinc soaps has been prepared by direct react with zinc oxide at 140 ℃ and stop heating after 2 hours. A small amount of water is added as a catalyst of the reaction.

3.2 Characterization of zinc soaps containing unsaturated fatty acids

3.2.1 Determination of Acid Value

Acid value is a measure of the quantity of free fatty acids and is defined as the number of milligrams of potassium hydroxide required to neutralize the fatty acids in 1 g sample. To determine the volume of KOH needed to titrate the solvent.

0.3 g of sample was weighed into the flask and add 50mL of acid value solvent (2:1 ethanol/toluene). If the sample is not dissolved, heat gently to dissolve it. Once the sample was dissolved, cool to room temperature under running water. 4 –5 drops of phenolphthalein was added and titrated to a faint pink color with 0.1N KOH. Total volume of KOH used been recorded. The test was repeated with a blank sample.

Calculation

$$Acid\ Value, \% = \frac{5.6\ (Sample\ of\ titrate, mL - Blank, mL)}{Weight\ of\ sample, g}$$

... Equation 1

3.2.2 Determination of Iodine value

This method covers the Wijs procedure for determination of unsaturation (iodine value) in all natural and synthetic drying oils and their fatty acids. When the iodine value is determined on oils or fatty acids having conjugated systems, the result is not a measure of total unsaturation, but rather is an empirical value that affords a comparison of total unsaturation.

A measured volume of Wijs iodine solution is reacted with a weighed sample in chloroform medium. Iodine is liberated from the unreacted Wijs solution with potassium iodide and titrate with sodium thiosulfate, using starch solution near the end point.

0.3g of sample was weighed and allow the sample to melt on the hot plate. Once melted, remove the sample from the hot plate and 20mL of chloroform was added. The sample cooled to ambient temperature.25mL of Wijs solution was pipetted into the flask containing the sample. A blank sample was prepared. The flasks were stopped and allow to store in the dark box for 2 hours at 25 ± 5°C.

The flasks were removed from storage and 20mL of KI solution and 100mL of

distilled water was added subsequently. 0.1N $Na_2S_2O_3$ solution was titrated gradually and with constant shaking. Continue the titration until the yellow colour has almost disappeared.

1 – 2mL of starch solution was added and continue the titration until the blue colour has just disappeared. The amount of titrant used was recorded. A blank test was carried out simultaneously under the same condition.

Calculation

$$Iodine\ Value, \% = \frac{(Blank, mL - Sample\ Titrate, mL)\ x\ 12.69}{Weight\ of\ sample, g}$$

... Equation 2

3.2.3 Determination of zinc soaps by using Gas chromatography Mass Spectroscopy

3.2.3.1 Sample preparation

<u>BF_3 Derivatization</u>

50 mg of sample was weighed into a test tube with stopper. 3 mL of BF_3 – Methanol was added. The test tube was capped. The sample shaked in few seconds. The sample should totally dissolve in BF_3 - Methanol. The test tube heated in a water bath around 70 -75 ℃ for 10 minutes. The test tube was removed from the water bath, cooled and added 5 mL of Hexane into the tube. The test tube was gently shaked by inverted it a few times. 1mL of saturated Sodium Chloride was added. Let the test tube stand until

two layers are formed. Took the upper layer (Hexane part); and transferred into a new test tube and added Sodium Sulphate Anhydrous to remove all trace of water.

Sodium Sulphate Anhydrous should be added until the Hexane layer is clear and not murky. After the Sodium Sulphate Anhydrous settle, took about 500 µL of this sample (Hexane layer) and diluted with another 500 µL of hexane. The sample injected into GC.

Silylation Derivatization

An aliquot of sample (40mg) is reacted with 1mL silylation reagent (BSTFA/ MSTFA : 4:1) and 1mL of pyridine. The derivatization ensures that even substances with functional groups such as alcohols and carboxylic acids are determined. The sample was analyzed by Gad Chromatography Mass Spectroscopy.

3.2.3.2 Instrumentation

Analytical instrument employed for the hydrocarbon analysis was GC-MS system from Shimadzu GC-2010 system coupled to mass spectroscopy detector. Poly (5%-diphenyl-95%-dimethylsiloxane) fused silica column (BPX 5 from Thermo Fisher) with 30 m length, 0.25 mm inner diameter and 0.10 µm film thickness was used for separation. Helium was used as the carrier gas. Table 3.1 shows the instrument settings used for the GC-MS analysis.

Table 3.1: Shimadzu 2010 GC-MS instrument set-up

Parameter	Setting
Injector temperature	300 ℃
Injection mode	Splitless
Sample injection volume	3 µL
Column flow	1 mL/min
Column mode	Constant flow
Septum purge flow	1 mL/min
Initial column temperature	40 ℃
Initial Time	1 min
Temperature ramp	15 ℃/min
Final temperature	300 ℃
Total run time	Approximately 40 min
MS interface temperature	300 ℃
Solvent delay	6.0 min
Ion source	Electron ionisation
Electron energy	70 eV
Ion source temperature	230 ℃
Mass analyser	Quadrupole
Quadrupole temperature	150 ℃
Mass range	33-700 amu
Scan time	1.14 scan/s
Mass detector	Electron multiplier

3.2.4 Determination of melting point

This method was used to determine the melting point of zinc soaps containing unsaturated fatty acids.

3.2.4.1 Sample preparation

The sample preparation is a very important part of a melting point test. Sample can occur in various crystal modifications with different melting points. To obtain reproducible and comparable measured values with pre-melted samples, it is absolutely essential to ensure that the same conditions are maintained on heating and cooling. Heat the sample, constantly stirring until it has become sufficiently fluid to pour. Pour the sample into a specimen cup. Allow to harden and cool to room temperature. The specimen cup is then placed in the cartridge and inserted in the Mettler FP80 system.

3.2.4.2 Instrumentation

The sample cup was placed in the cartridge which heated in the Mettler FP 80 system. The fall of the first drop was recorded photoelectrically and the temperature at which this occurs was recorded and displayed.

Figure 3.1: Device to measure the melting point.

3.2.5 Determination zinc content by using MP-AES

3.2.5.1 Sample preparation

0.5g of sample was weighed into the 250mL beaker. 50mL of concentrated nitric acid was added into the beaker. The beaker closed with the watch glass. The sample was heated until all the sample fully digested into the acid solution. The solution was transferred into 100mL volumetric flask and water was added mark up to 100mL.

3.2.5.2 Instrumentation

All measurements were performed using an Agilent 4200 MP-AES. Dewar nitrogen was used to run the MP-AES. Nitrogen can be supplied using either bottled gas or an Agilent 4107 Nitrogen Generator. A multi-purpose sample introduction system configuration was used with an inert OneNeb nebulizer and a double pass glass cyclonic spray chamber, orange/green pump tubing and a pump speed of 10 rpm. This setup provided a well-controlled matrix loading to the plasma without sacrificing detection limits. The nebulizer gas flow is mass flow controlled, providing short and long-term sample nebulization stability during the high total dissolved solid sample analysis. The

instrument operates in a fast sequential mode and with the peltier cooled CCD detector, background and spectral interferences can be simultaneously corrected easily and accurately using MP Expert software. The method parameters are given in Table 3.1.

Figure3.2: Microwave plasma atomic emission spectroscopy.

Table 3.2: Agilent MP-AES 4100 instrument set-up

Parameter	Setting
Nebulizer	OneNeb
Nebulizer flow	0.4 mL/min
Spray Chamber	Double pass glass cyclonic
Pump rate	10 rpm
Sample pump tubing	Green
Read time	15 seconds
Number of replicates	3
Fast pump during uptake	On
Sample uptake	Delay 30 minutes
Rinse time	120 seconds
Stabilization time	20 seconds
Background correction	On

3.2.5.3 Calibration standard solution

In order to quantify the zinc that presents in the samples, calibration using zinc standard was carried out. The calibration plot was established using 2, 4, 6, 8 and 10 mg/L zinc standard as shown in Table 3.2. This check standard was prepared from a 1000 mg/L standard solution (Merck, ICP grade).

Table 3.3: Standard calibration with different concentration.

Calibration Concentration, ppm	2	4	6	8	10
Standard Solution , mL	0.2	0.4	0.6	0.8	1.0
DI Water, mL	99.8	99.6	99.4	99.2	99.0

3.2 Performance testing on rubber compounds

3.3.1 Spiral Flow Test

A spiral flow analysis based on the McLean-Anderson design method was conducted study the influence of each formulation component on the flow of rubber. The spiral flow distance (SFD) of formulation as a function of ingredient concentration was measured and analyzed. (Hsu, 1995). This is a simple, inexpensive, well established to determine of flow properties under moulding conditions. A three part spiral moulds which can be manually operated is used in a laboratory press (Figure 3.3).

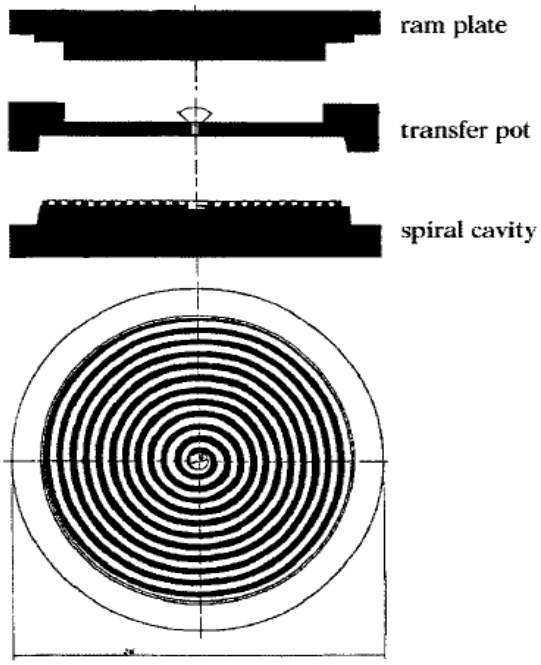


Figure 3.3: Spiral Moulds (Struktol,2004)

Rheometer test was run on rubber compound at 150 ℃ to determine the compound TC90 cure time. The mould was pre-heated and the cure time of the press machine was set according to rheometer TC90 + 1 minute. After the mould reached to the set temperature, rubber compound placed between top and bottom platen. “START” button was pressed and started the curing. After completed the vulcanization process, the spiral vulcanizate took out at the bottom plate and weighed it to compare compound the flow performance. The test was repeated with a control sample.

Figure 3.4: Spiral mould for flow test

3.3.2 Blooming Test

A discolouration or change in the appearance of the surface of the Rubber due to the migration of solid or liquid materials/substances, is termed as blooms in rubber. Bloom analysis can be done by examination of the surface as it stands or to attempt to remove any bloom present and carry out a subsequent analysis on the separated bloom.

The rubber with the sample was prepared. The rubber putted into room temperature and observed visually after a week. If white particles appeared on the rubber, is mean the blooming effect occurred.

3.3.3 Tensile Properties

The tensile slab was prepared and conditioned it for minimum 24 Hours after vulcanization and it should be kept in a room maintained under standard conditions for not less than 1 hour before test. Dumbell Cutter-Type-C was used to cut the sample. The dumbell was installed at Tensiometer Grip. The dumbell information keyed into software system before started the test. 'Zero Force' & 'Zero Disp' buttons were pressed and tarred the value into zero. The test was started and stopped it until the sample broke. 3 samples was run with consistent results. The testing was repeated with the blank sample.

Figure 3.5: Tensile strength equipment to use measure the tensile properties.

3.3.4 Hardness

TECLOCK Durometer was installed to Constant Pressure Stand. The guide bar was adjusted to get required high Lift durometer with Lever. The hardness button sample was pressed on Test Table. The Lever was lowed to get the hardness value. The value was took after the value is stable. 3 points of measurement was took and averaged the test results. The testing was repeated with blank sample.

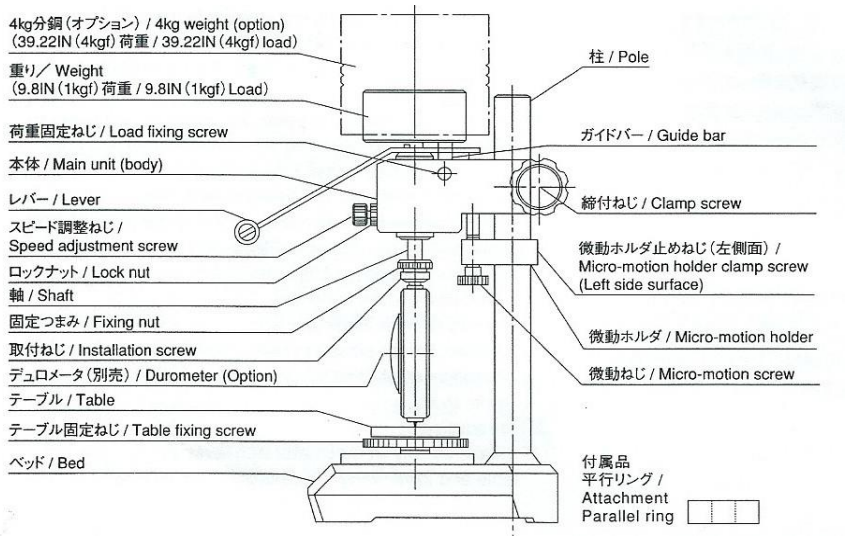


Figure 3.6: Durometer to measure the hardness of the rubber compounds.

3.3.5 Carbon Black Dispersion

The Carbon Black Dispergrader was turned on at least an hour. The rubber sample was placed on the centre of the test platform. The carbon black dispersion software opened to get U-CAN video capture utility. The microscope lens in/out was adjusted to get the best view. ‘Capture’ botton was pressed and continoued pressed '10 Rating CHK' to evaluate the carbon black dispersion. The testing was run with blank sample.

Figure 3.7: Carbon black dispersion measurement device.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Determination of Acid Value

Table 4.1: Acid value of the palm based zinc soaps.

Number of sample	1	2	3	4	5	Average
Acid Value, mgKOH/g	159.23	158.41	159.74	158.44	158.92	158.95

The acid number is used to quantify the amount of acid present in the sample. The acid value is high and due to unsaturated soap.

4.2 Determination of Iodine value

Table 4.2: Iodine value of the palm based zinc soaps.

Number of sample	1	2	3	4	5	Average
Iodine Value, gI_2/100g	55.50	55.30	54.80	54.70	55.30	55.12

In analytical chemistry, iodine value is estimate the unsaturation of the product. The more iodine is attached, the higher is the iodine value. The soap is containing saturated and unsaturated fatty acids. It can be classified into saturated or unsaturated based on the number of double bonds present in the fatty acid. Saturated fatty acids contain only single bond between the carbon atoms and are tend to be solids at room temperature. Unsaturated fatty acids contain double bonds between carbon atoms in addition to the single bonds present in the fatty acid chain.

The melting point increases when degree of unsaturation is high. In another words, the greater the number of double bonds present, the higher the melting point. Therefore, the percentage of unsaturated fatty acid soaps should under control. The soap is not suitable if containing too much unsaturated and will increase the melting point of the product although the unsaturated fatty acids can reduce the blooming effect in the rubber compounding. Besides that, a zinc soap of unsaturated fatty acids can reduce NR Mooney of 85 to 60 in about 2 minutes on a 2-roll mill at 80℃ and to Mooney 50 in about 4 minutes. Without the zinc soap, Mooney 50 was only achieved in 8 minutes. (Sin, 2000).

4.3 Determination of zinc soaps by using Gas chromatography Mass Spectroscopy

Silylation is the most widely used derivatization technique. Functional groups that present a problem with gas chromatogaphy detection - hydroxyl, carboxylic acid, amine, thiol, phosphate - can be derivatized by silylation reagents. Silylation involves replacement of the acidic hydrogen with an alkylsilyl group, for example, -$SiMe_3$.

Silylation derivatives are generally less polar, more volatile and thermally more stable. The choice of a silylating reagent is based on its reactivity and selectivity towards the compound, the intended application, the stability of the derivative, and the abundance/nature of reaction by-products.

There are four high intensity peaks show on the chromatogram. Hexadecanoic acid, Octadecanoic acid and Tetradecanoic acid are saturated fatty acids. The unsaturated fatty acid shows on the chromatogram, which is trans - 9 Octadecanoic acid. The

unsaturated fatty acid can reduce the blooming effects on the compounder. Figure 4.1 shows that gas chromatogram with distribution of Hexadecanoic acid, Tetradecanoic acid, Octadecanoic acid and Trans-9 Octadecanoic acid using silylation derivatization. Figure 4.2, 4.3, 4.4 and 4.5 show mass spectrums of the zinc soaps. The chemicals identified by their m/z ratios can be confirmed by their fragmentation pattern by mass spectroscopy.

BF_3-methanol is one of the fastest and most convenient ways to convert fatty acids to their methyl ester derivatives. The reagent is supplied in an easy-to-use, septum-sealed Hypo vial and offers convenient syringe removal of the reagent without exposing it to air. Use of the BF_3-methanol reagent results in improved detection of fatty acids in a fatty food matrix while maintaining good chromatographic peak shape. Figure 4.6 shows that gas chromatogram with distribution of Hexadecanoic acid, Tetradecanoic acid, Octadecanoic acid and Trans-9 Octadecanoic acid using BF_3-methanol derivatization. Figure 4.7, 4.8, 4.9 and 4.10 show mass spectrums of the zinc soaps using BF_3-methanol derivatization. The chemicals identified by their m/z ratios can be confirmed by their fragmentation pattern by mass spectroscopy.

Both derivatization methods show same chromatogram with distribution of Hexadecanoic acid, Tetradecanoic acid, Octadecanoic acid and Trans-9 Octadecanoic acid. The price of BF_3-methanol is cheaper than silylation reagent. The BF_3-methonol method will be used in future study.

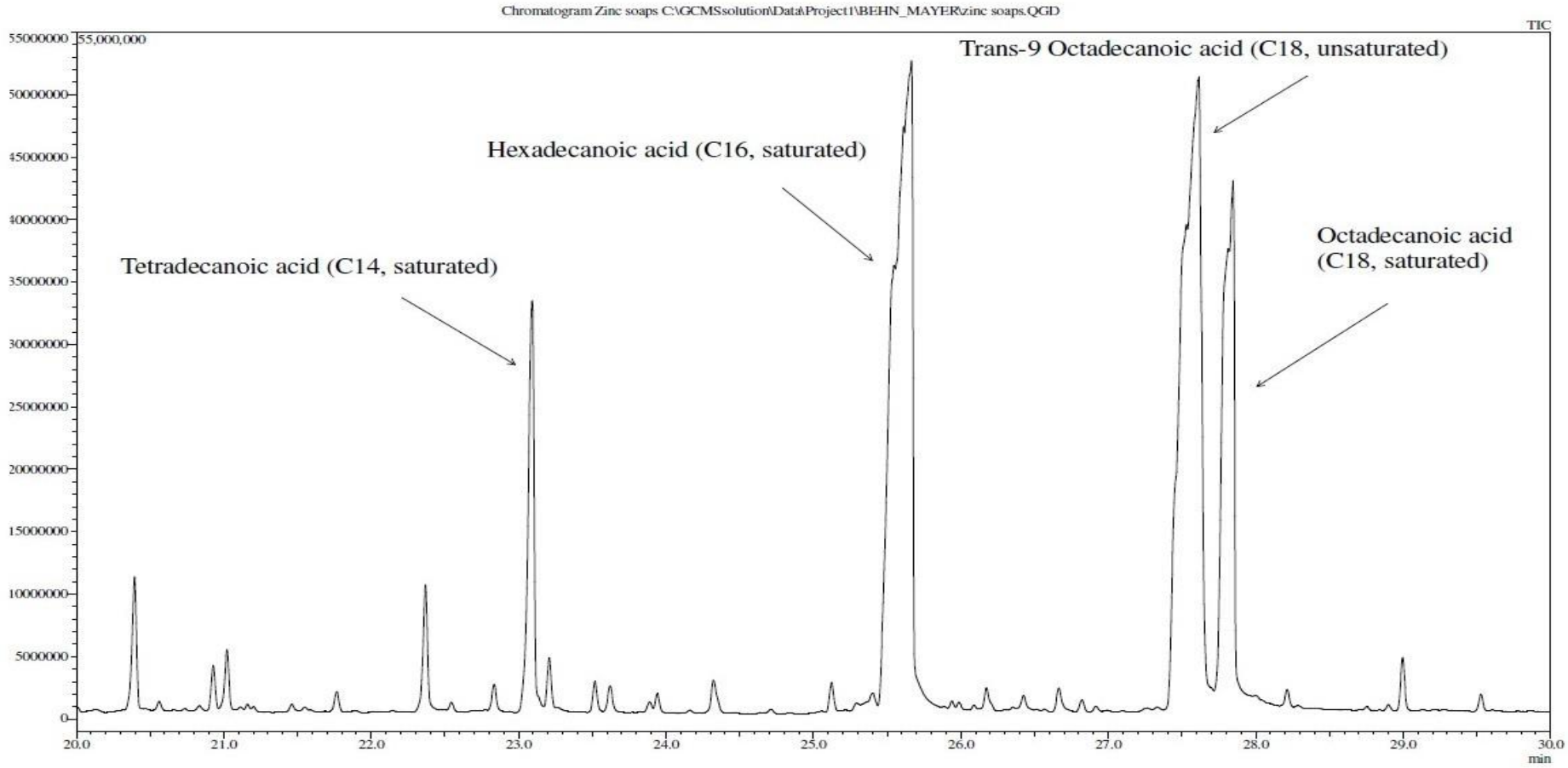


Figure 4.1: Gas chromatogram showing the distribution of Hexadecanoic acid, Tetradecanoic acid, Octadecanoic acid and Trans-9 Octadecanoic acid using silylation derivatization.

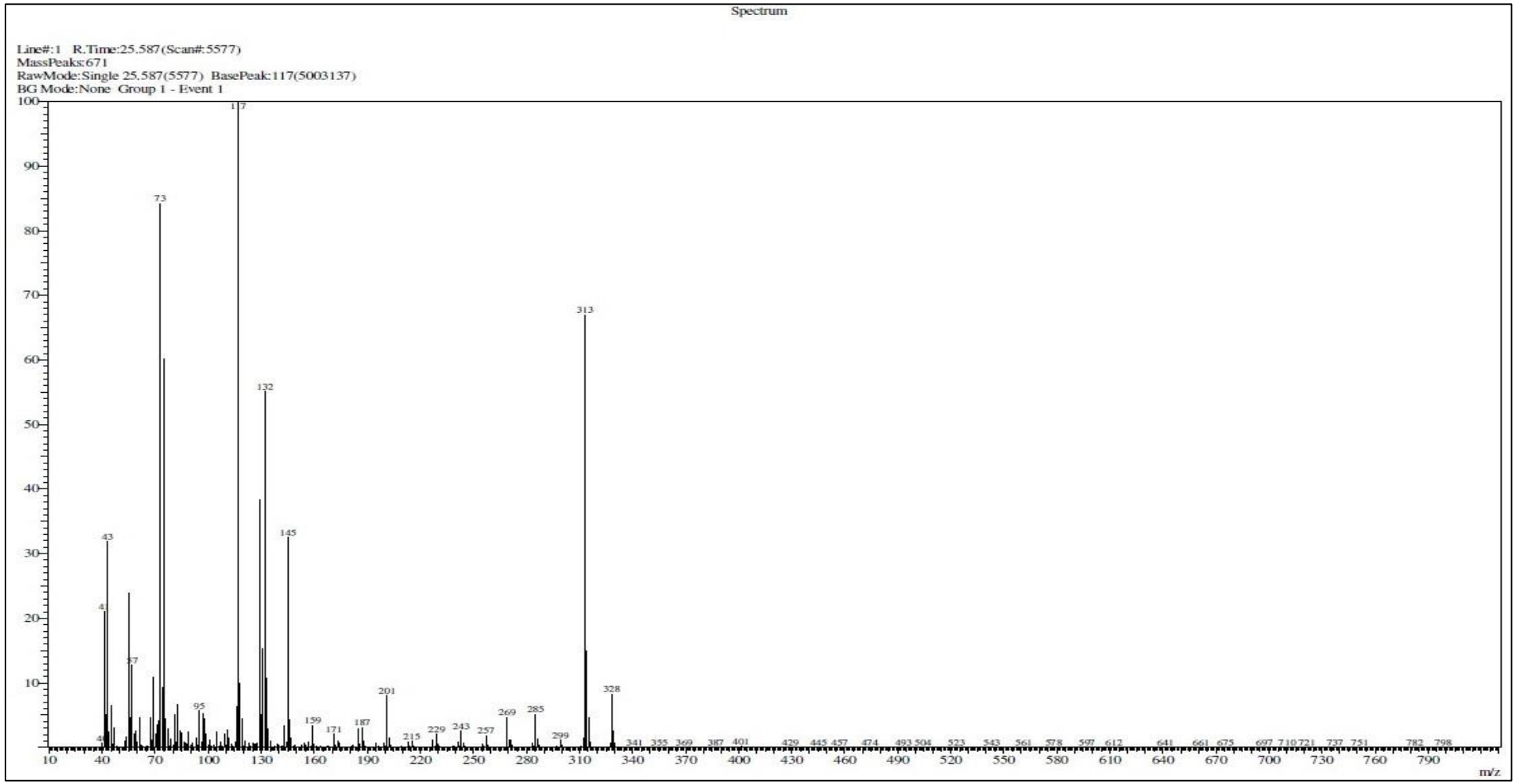


Figure 4.2: Mass spectrum of the Hexadecanoic acid (Silylation method).

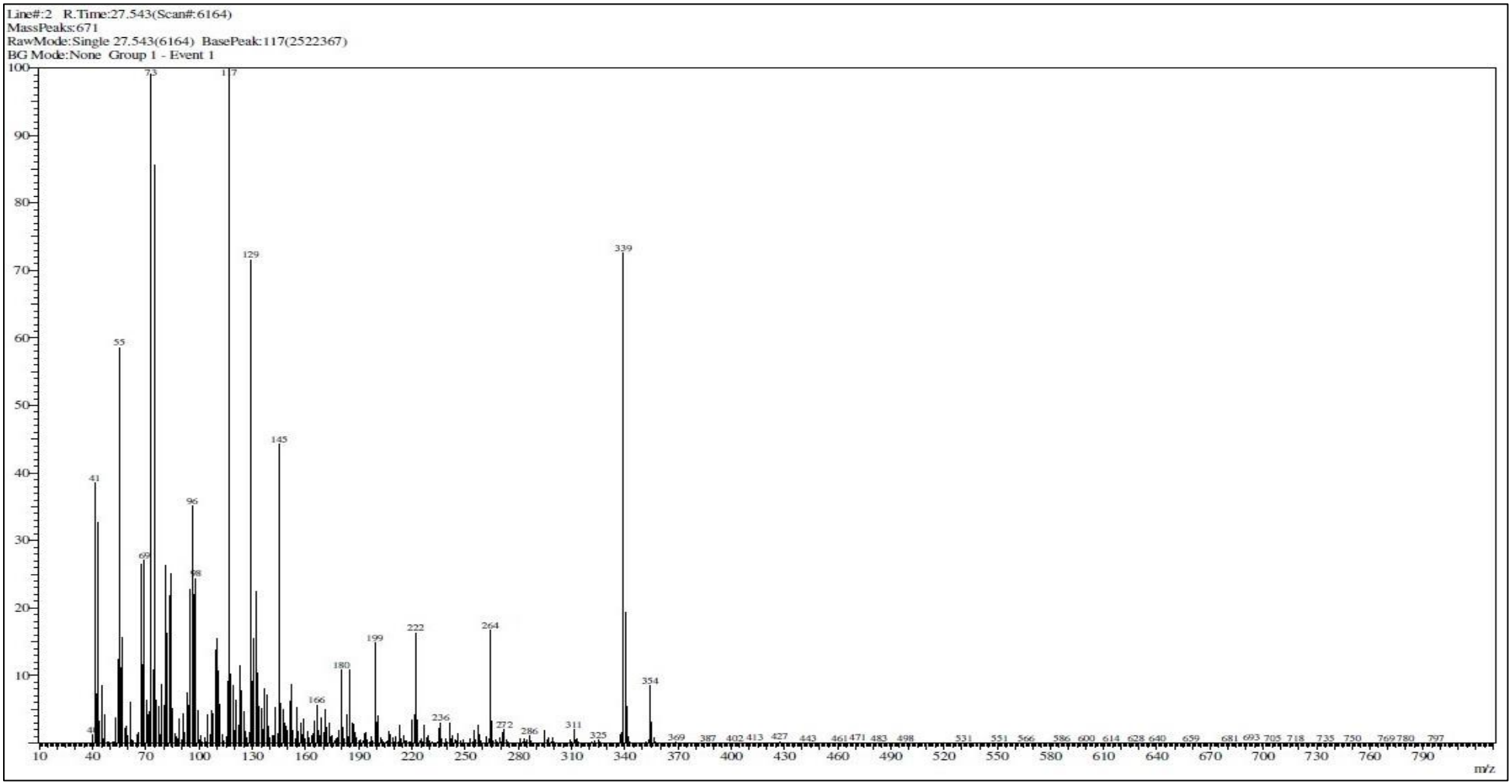


Figure 4.3: Mass spectrum of Tetradecanoic acid (Silylation method).

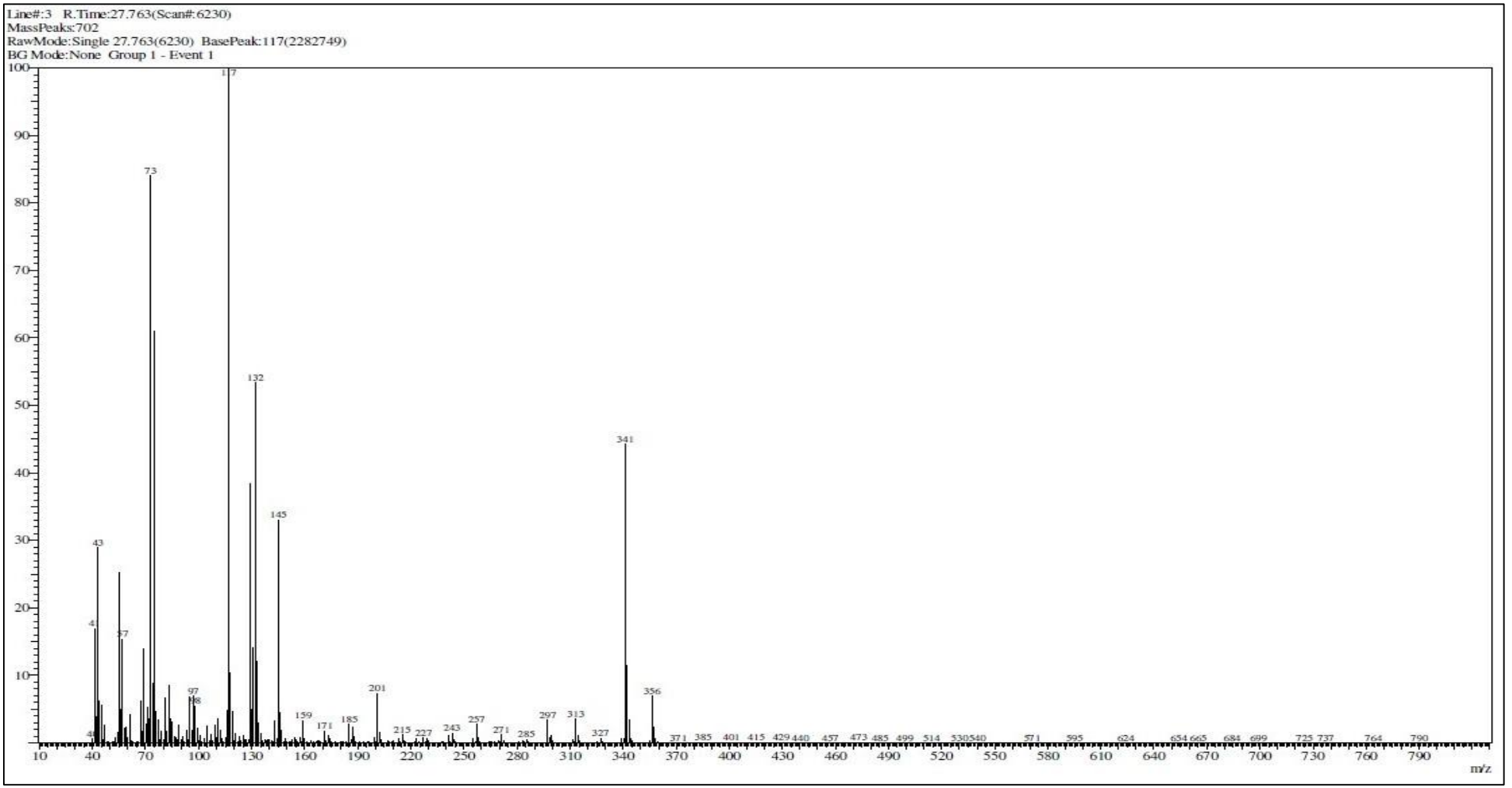


Figure 4.4: Mass spectrum of Octadecanoic acid (Silylation method).

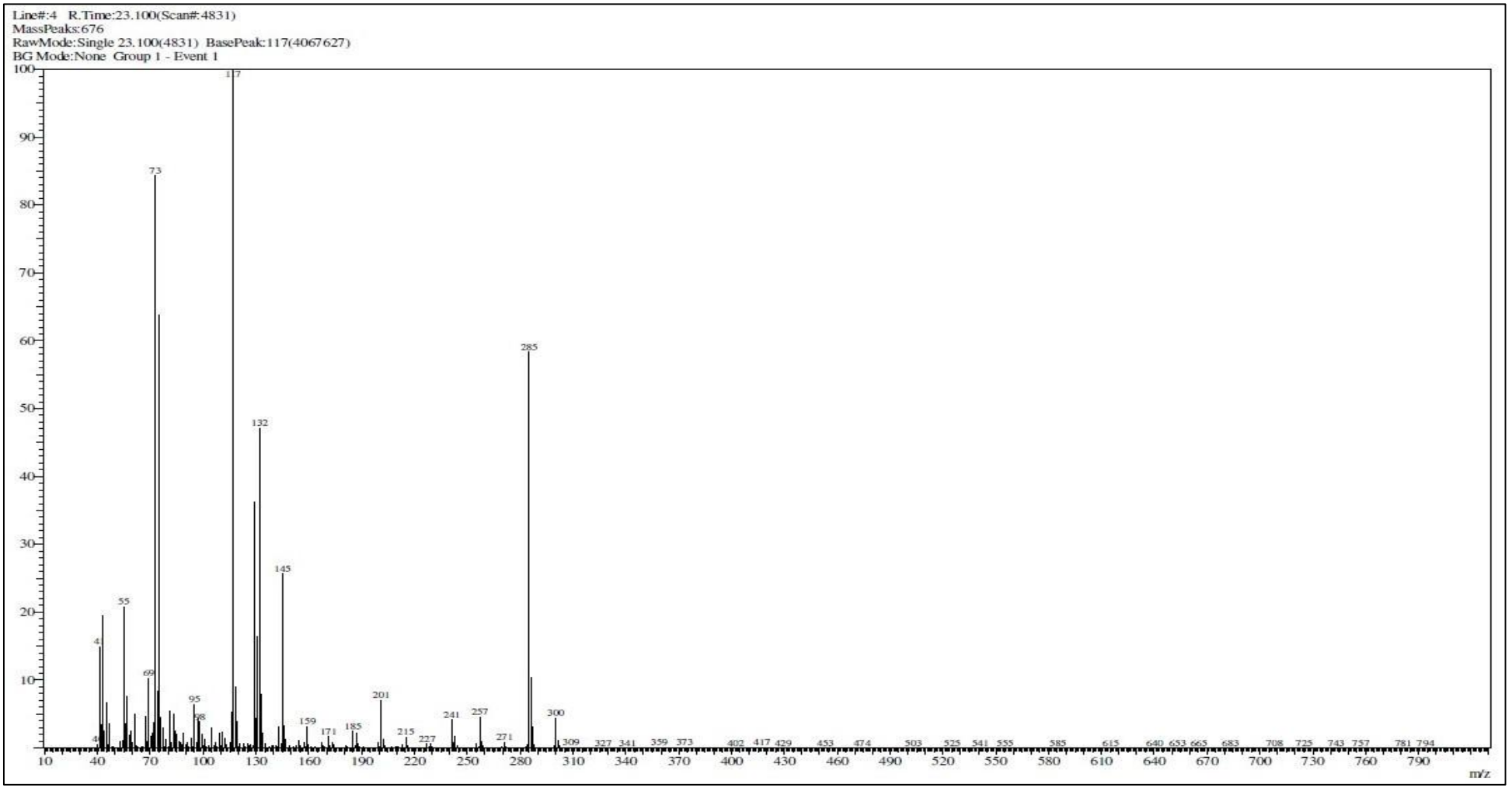


Figure 4.5: Mass spectrum of Trans-9 Octadecanoic acid (Silylation method).

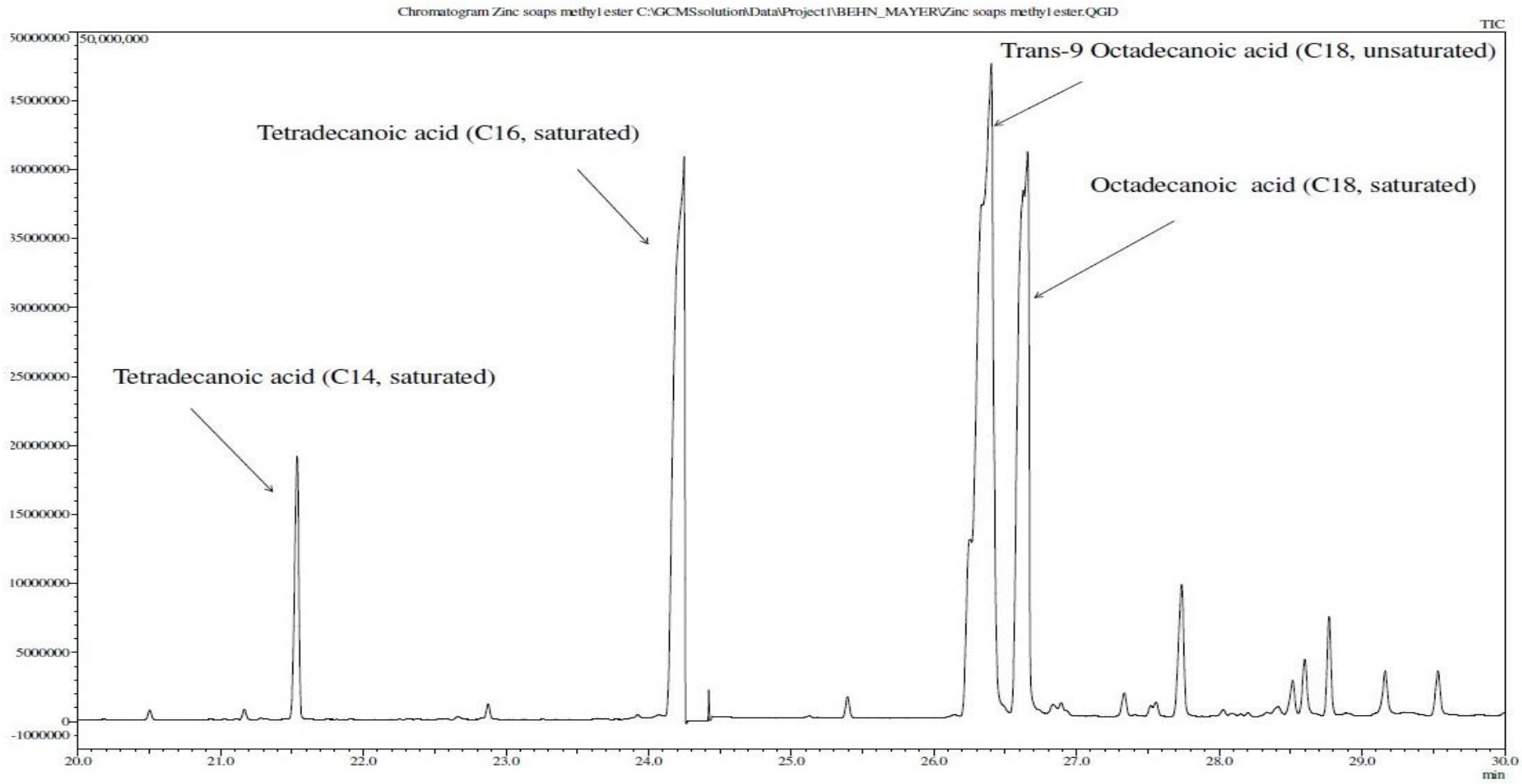


Figure 4.6: Gas chromatogram showing the distribution of Hexadecanoic acid, Tetradecanoic acid, Octadecanoic acid and Trans-9 Octadecanoic acid using BF_3 derivatization.

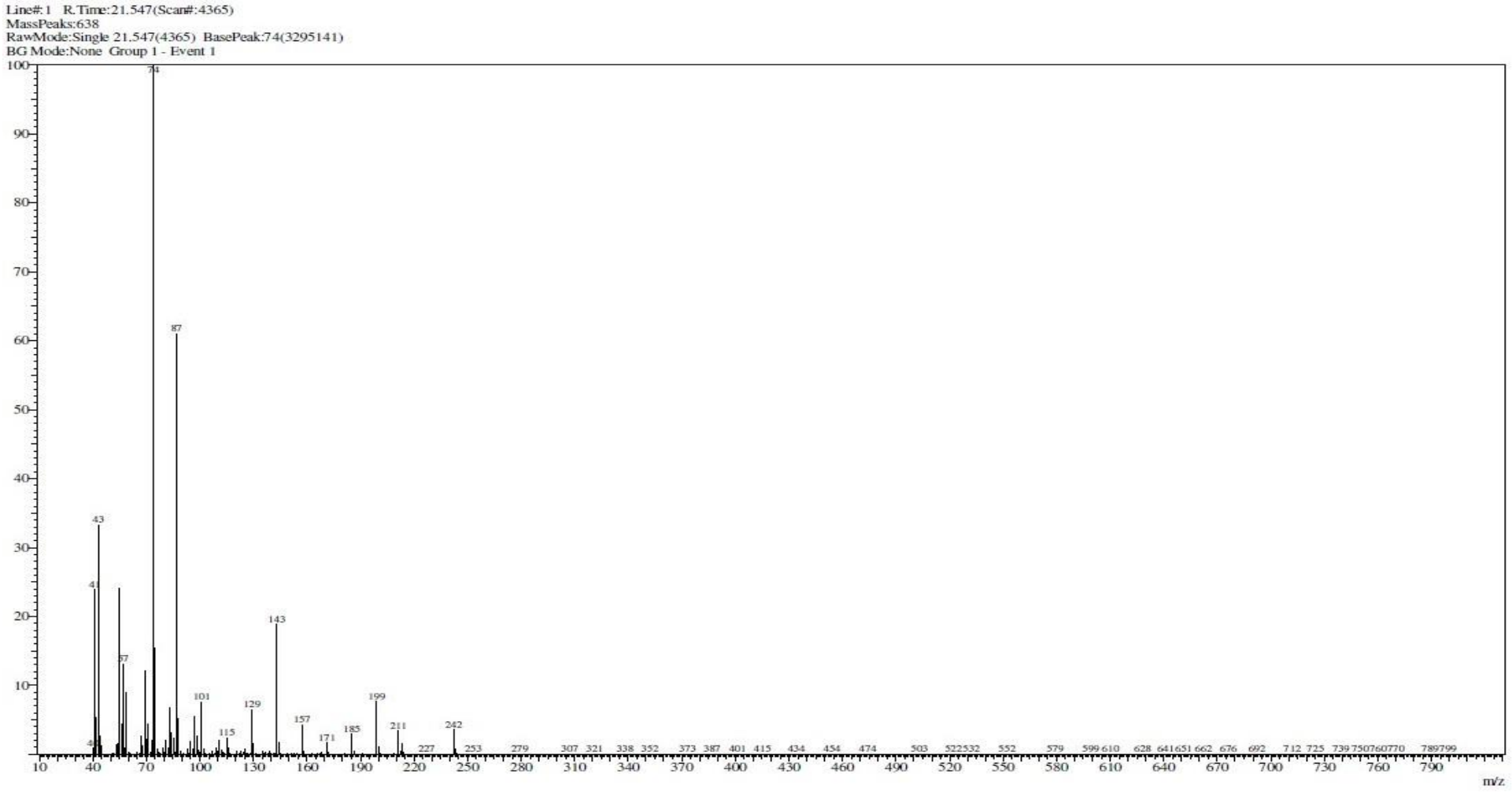


Figure 4.7: Mass spectrum of the Hexadecanoic acid (BF_3 derivatization method).

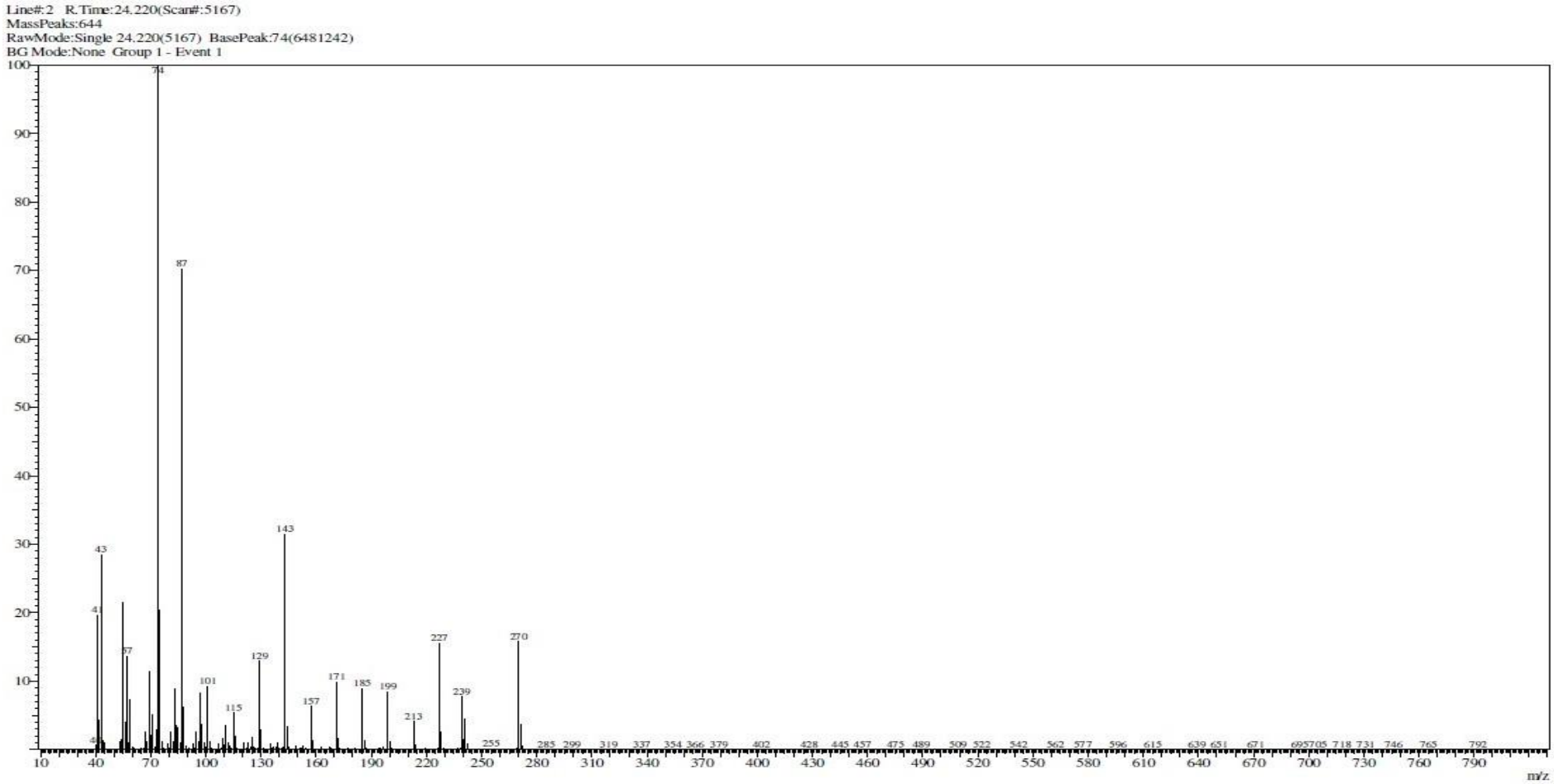


Figure 4.8: Mass spectrum of the Tetradecanoic acid (BF_3 derivatization method).

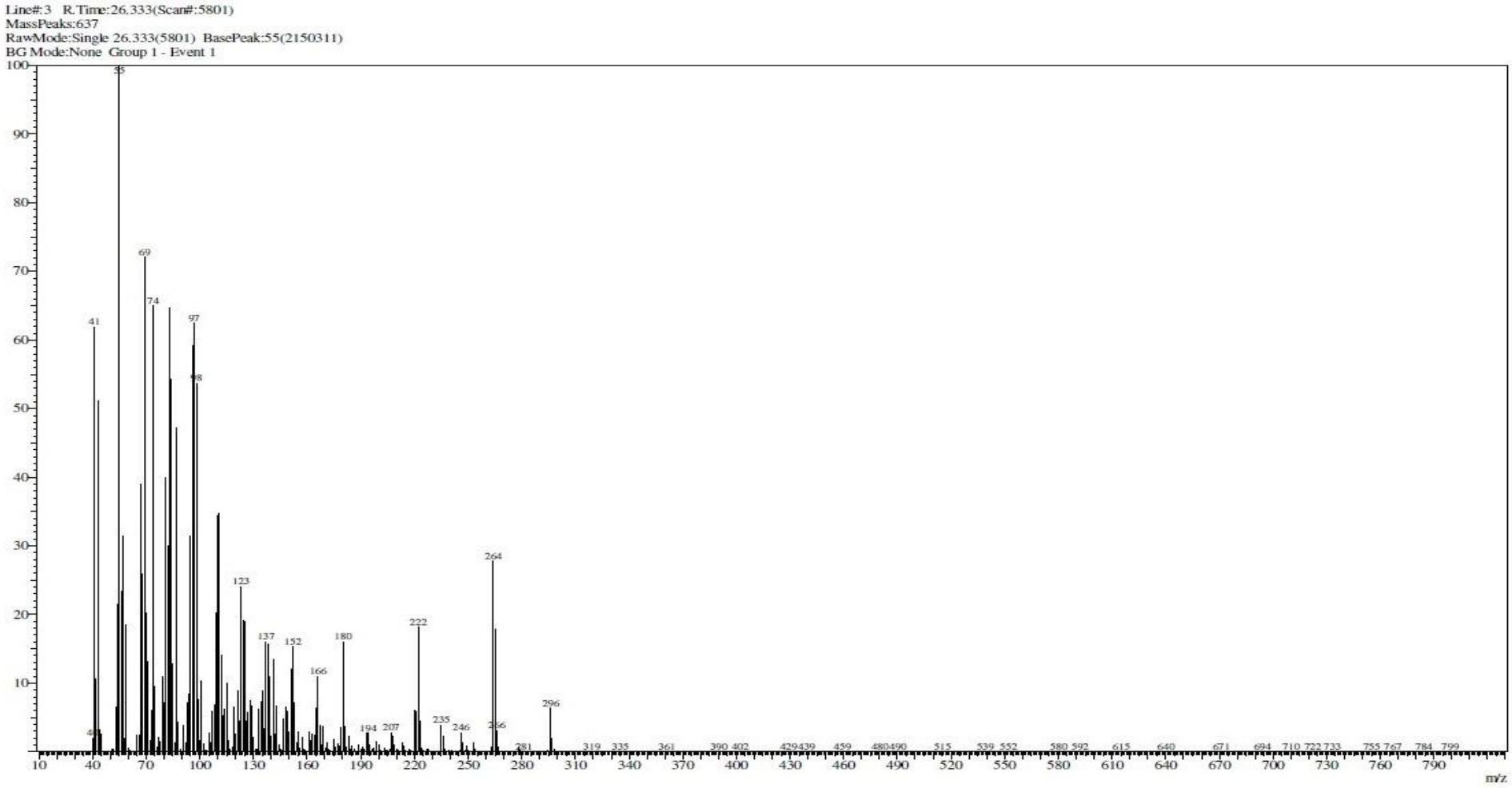


Figure 4.9: Mass spectrum of Octadecanoic acid (BF_3 derivatization method).

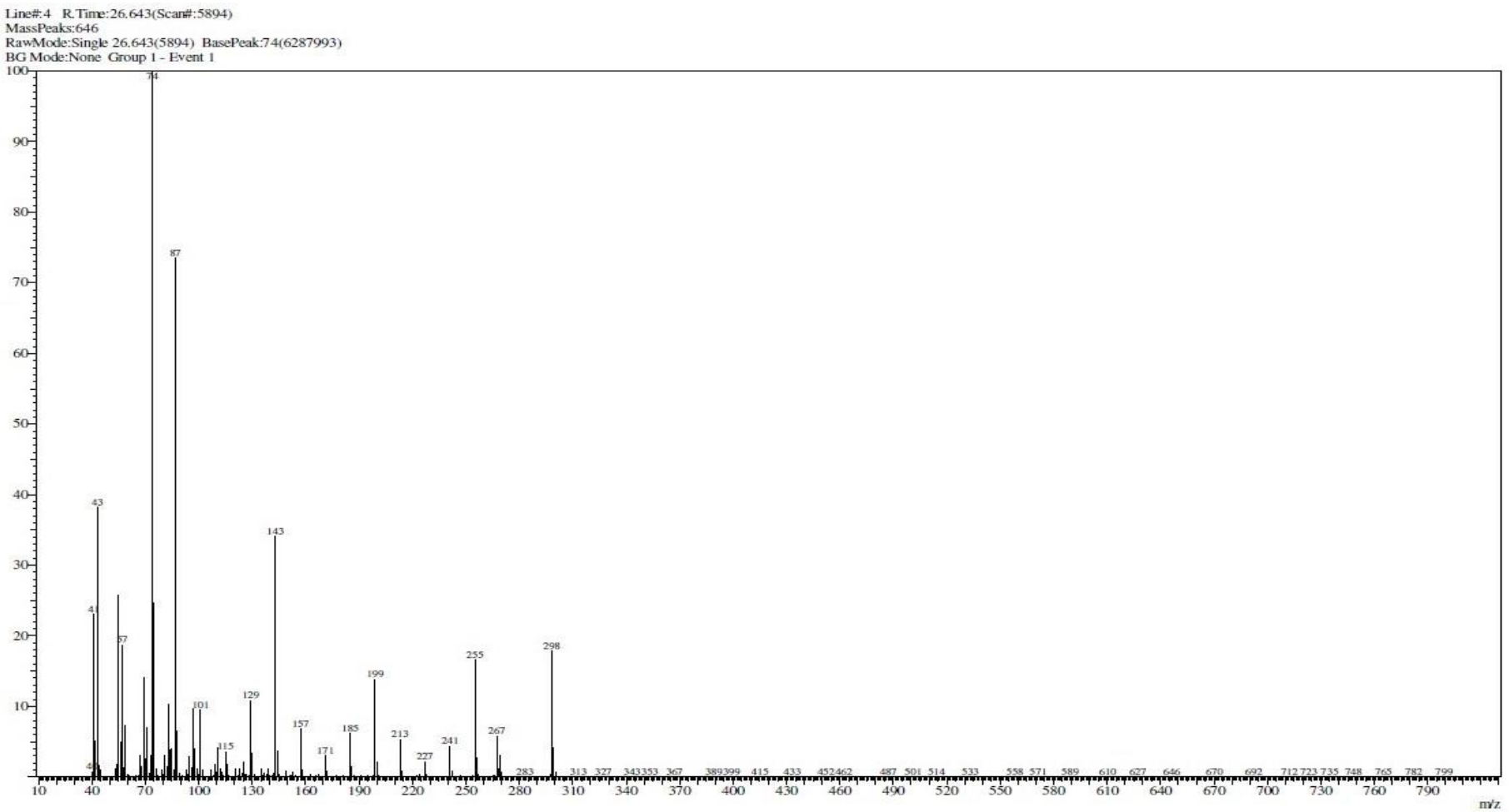


Figure 4.10: Mass spectrum of Trans-9 Octadecanoic acid (BF_3 derivatization method).

4.4 Determination of melting point

Table 4.3: Melting point of the palm based zinc soaps.

Number of sample	1	2	3	4	5	Average
Melting Point, ℃	100.1	100.2	100.1	100.0	100.2	100.1

The melting point of the synthesis sample is much lower than the zinc stearate which is normally in range of 120-130 ℃. The result shows lower melting point and meet the objective of the project.

In addition to the normal (straight chain) saturated acids, there occur several with hydroxyl groups, and/or one or more double bonds in the carbon chain. The presence of unsaturation (double bonds) in soap tend to lower the melting point of these compound. The double bonds lower the melting point of a fatty acid chain as the chain attached to the double bond are attached cis-wise to each other. These probably because the double bond cis configuration produces a bent chain which does not easily adhere to a neighbouring chain by a Van der Waals attraction hence a lower temperature (lower mobility) is required for these molecules to adhere in order to form a solid crystal lattice. It is interesting to note, that straight chained carboxylic acids having an odd number of carbon atoms melt lower than even chained acids of comparable molecular weights (Walter Scharf, 2010).

The melting point is a main factor of which metallic soap to use on the rubber compounds. When the rubber compounder is making stock for transfer moulding, compression, extruded profiles or hoses, the cure temperature or moulding and time duration will limit to the materials on the surface of the compound. With a lower

melting point of processing additives, the rubber compounds can mix in a lower temperature and reduce the curing temperature.

4.5 Determination zinc content by using MP-AES

Table 4.4 is the data obtained from the calibration using zinc standard, and the calibration curve is shown in Figure 4.11. Coefficient of determination, R^2 value of 0.99825 was obtained for the standard at the concentration from 0.4 ppm to 2.0 ppm. This shows that a good linear correlation was achieved.

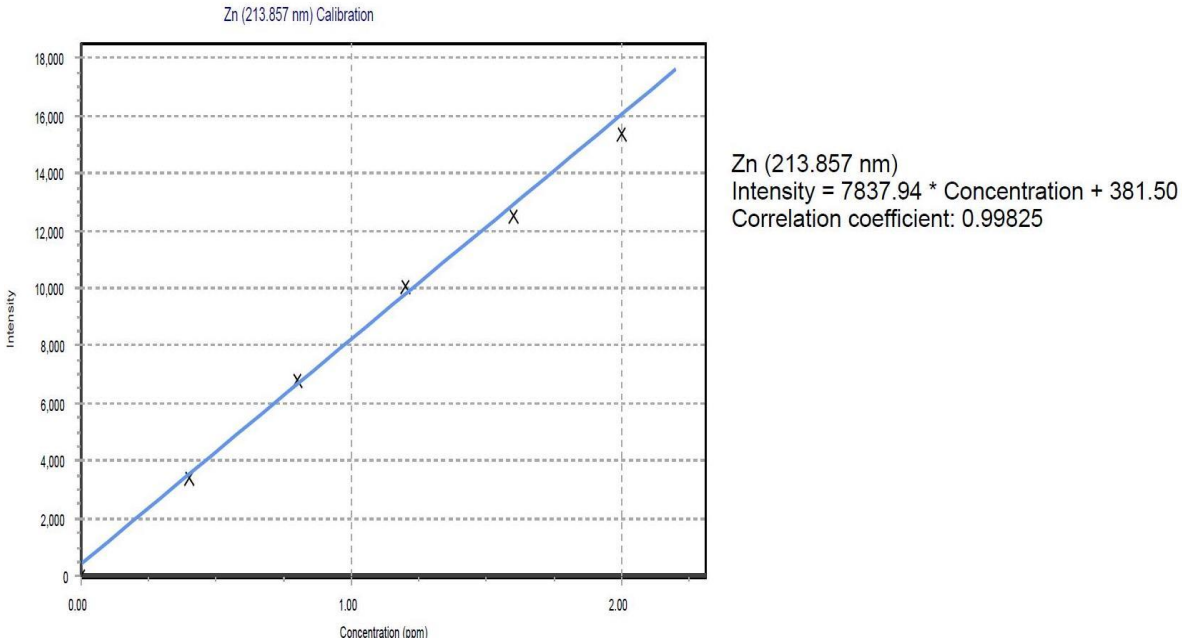


Figure 4.11: Calibration curve for zinc standard, ranging 0.4 to 2.0ppm.

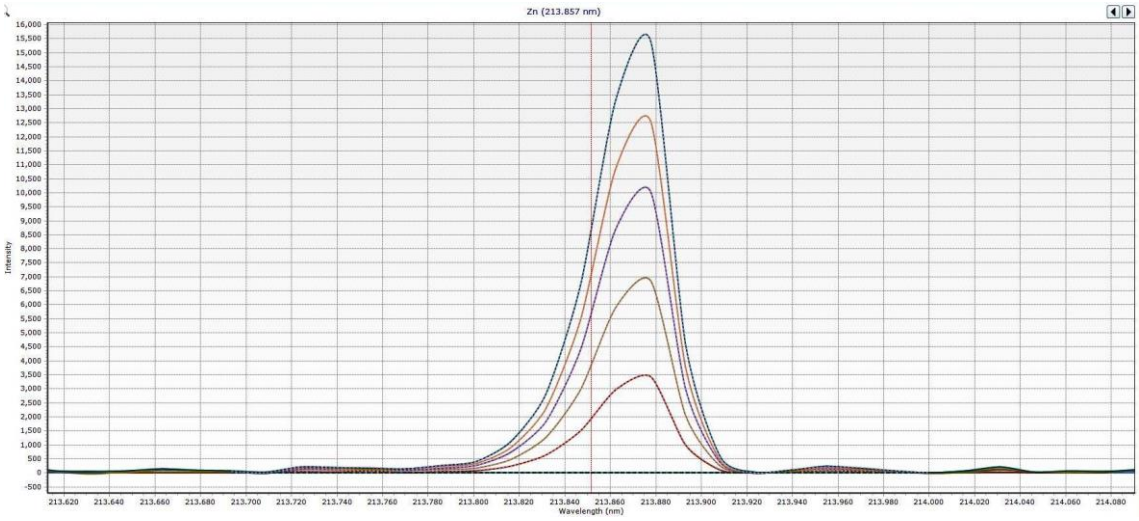


Figure 4.12: Overlay of 0.4 to 2.0 ppm of zinc standard (213.857 nm).

Table 4.4: Calibration results of zinc standard, ranging 0.4 to 2.0 ppm.

Standard Concentration	Intensity	Actual Concentration	% Error
0.00	0.01	-0.01	N/A
0.40	3426.31	0.39	2.50
0.80	6835.04	0.82	2.50
1.20	10041.93	1.23	2.50
1.60	12542.60	1.55	3.13
2.00	15384.23	1.93	3.50

Table 4.5: Zinc content of the palm based zinc soaps.

Sample	Measured Zn concentration in sample, ppm	Measured Zn concentration in spike sample, ppm	Spike + material concentration , ppm	Recovery, %
1	1.08	2.00	3.03	95.37
2	1.04	2.00	3.01	97.12
3	1.07	2.00	3.03	96.26
Average:	1.06		Average Recovery, %	96.25

Calculation

$$Total\ zinc\ content, \% = \frac{(Concentration\ of\ the\ result)\ x\ Dilution\ factor}{Weight\ of\ sample, g}$$

$$= \frac{(1.06\ ppm)\ x\ 60000}{0.5078\ x\ 10000} = 12.5246\ \%$$

The dilution factor of the sample is 60000. Therefore, the concentration of the zinc content is 12.52%.

4.6 Spiral Flow Test

This test method covers a procedure for measuring the spiral flow of thermosetting moulding compounds under pressure of 6.9 MPa (1000 psi). It is especially suited for those compounds that may be used for encapsulation or other low pressure moulding techniques.

Three type of samples are used to conduct the test. The sample without add any processing additives is used as a control of the test. Higher of the value means the sample has a better of the flow ability. Sample with zinc stearate and zinc fatty acids soap show higher flow ability compare with the control sample. The zinc fatty acids soap has same flow ability with the zinc stearate.

Table 4.6: Comparison spiral flow test results of zinc soaps, control sample and zinc stearate.

Sample	Control (Without processing additives)	Zinc Stearate (2.5 phr)	Zinc fatty acids soap (2.5 phr)
Weight of mould flow, g	3.8	4.2	4.2

Figure 4.13 and Figure 4.14 show the comparison spiral vulcanize of different processing additives with the control sample. The weight of spiral vulcanize for both testing samples are higher than the control sample. The soap helps the rubber compound to flow smoothly. Therefore, more rubber compound flows out from the spiral plate. The length of spiral vulcanize of compounds with processing additives are longer compared with the control sample.

Figure 4.13: Comparison spiral vulcanize of compound using zinc stearate with control sample.

Figure 4.14: Comparison spiral vulcanize of compound using zinc fatty acids soap with control sample.

4.7 Blooming Test

The surface of rubber compound of control sample (Figure 4.15) looks clear and without any white spots. But, the surface of rubber with zinc stearate (Figure 4.17) are found with a lot of white spots. The rubber compound with zinc soaps looks clear but still a few white spots appear on the surface of rubber (Figure 4.16).

Since most rubber chemicals are more polar than NR, they do dissolve at high temperature during compounding and form a super saturated solution. Once it is cool

down in room temperature, these chemicals will bloom out and give an off white matt on the surface of rubber compound.

Zinc stearate bloom usually occurs due to excessive use of zinc stearate or separation of rubber with zinc stearate in a certain period of time. It is generally recognized because zinc stearate is not completely soluble in the base elastomers and may separate out with time.

Zinc soap which containing unsaturated fatty acids is more stable. A double bond of fatty acids. Zinc soaps of branched or aromatic carboxylic acids are soluble in rubber. They provide substantial improvement in creep and modulus reproducibility compared with zinc stearate. Bloom that occurs with uncured stocks can cause downstream problems in the factory, such as loss of building tack. Bloom that appears on the cured product will cause problems with the customers.

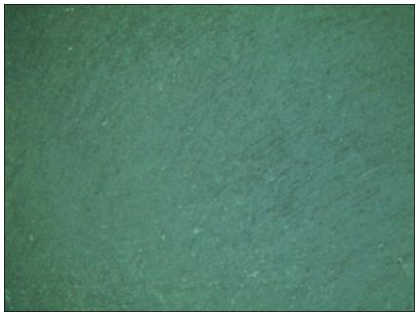


Figure 4.15: A surface of rubber compound without use any processing addtives.

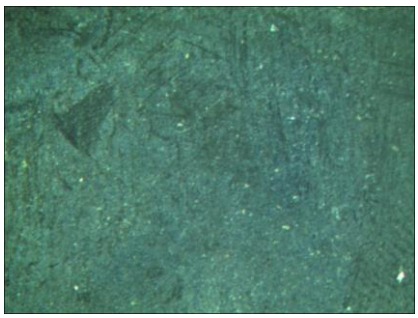


Figure 4.16: A surface of rubber compound use zinc soaps.

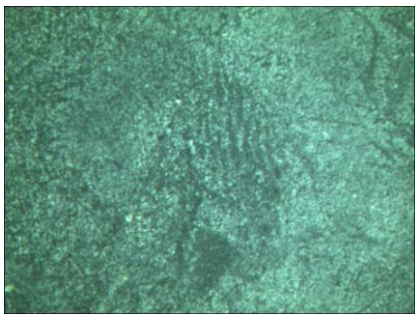


Figure 4.17: A surface of rubber compound use zinc stearate.

4.8 Tensile Properties

Table 4.7: Comparison tensile properties of rubber compounds using zinc soaps and zinc stearate.

Sample	Control (Without processing additives)	Zinc Stearate (2.5 phr)	Zinc fatty acids soap (2.5 phr)
Tensile Strength, Mpa	20.33	20.51	20.48

Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. Tensile tests are used to determine the modulus of elasticity, elastic limit, elongation, proportional limit, and reduction in area, tensile strength, yield point, yield strength and other tensile properties. The results show that the zinc fatty acids soap has no improvement tensile effect to the rubber compounds. In other words, it will not reduce the tensile properties of the rubber compounds, is suitable for use as a processing additives.

4.9 Hardness

Table 4.8: Comparison hardness of rubber compounds using zinc soaps and zinc stearate with control sample.

Sample	Control (Without processing additives)	Zinc Stearate (2.5 phr)	Zinc fatty acids soap (2.5 phr)
Hardness, Hs	64	64	64

Durometer is a term for hardness as indicated by the Shore durometer number. The normal range for isolation materials is 40 to 60 ± 5 as limited by dynamic stiffness. Dynamic stiffness increases with hardness and in broad terms, the filler ratio of the materials to the rubber content as well as the carbon black reinforcement, plasticizers etc.

The results obtained from this test are useful as a measure of relative resistance to indentation of rubber. However, the Durometer hardness test does not serve well as a predictor of other properties such as strength or resistance to scratches, abrasion, or wear and should not be used alone for product design specifications. Shore hardness is often used as a proxy for flexibility (flexural modulus) for the specification of elastomers. The correlation between Shore hardness and flexibility holds for similar materials, especially within a series of grades from the same product line, but this is an empirical and not a fundamental relationship. The results show that zinc fatty acids soap has no effect for rubber compounds.

4.10 Carbon Black Dispersion

Table 4.9: Comparison carbon black dispersion of rubber compounds using zinc soaps and zinc stearate with control sample.

Sample	Control (Without processing additives)	Zinc Stearate (2.5 phr)	Zinc fatty acids soap (2.5 phr)
Particle	655	335	289
Particle area	38891.531	18088.513	16576.638
Max Particle Diameter	35.289	33.517	28.710
Agglomerations	351	182	180
Ave Particle Size	59.50	54.01	57.42
Ave Particle Diameter	8.702	8.291	8.549
Particle Rate, %	2.579	1.200	1.099
Dispersion, %	90.81	95.30	95.95

Table 4.9 shows that comparison carbon black dispersion of rubber compounds using zinc soaps and zinc stearate with control sample. The carbon black easily agglomerate if without any processing additives. The carbon black dispersion of rubber compounds using zinc stearate and zinc fatty acids show same result in agglomerations and particle size. In other words, both samples show same dispersion performance on the rubber compounds. Figures 4.18, 4.19 and 4.20 show the carbon dispersion of the rubber compounds. The white spots show in Bilivel picture are carbon blacks. The white spots populated in certain area only for control sample. It means the carbon blacks do not disperse homogenously in the rubber compounds. The white spots disperse homogeneous if added some processing additives are added.(Figure 4.19 and Figure 4.20)

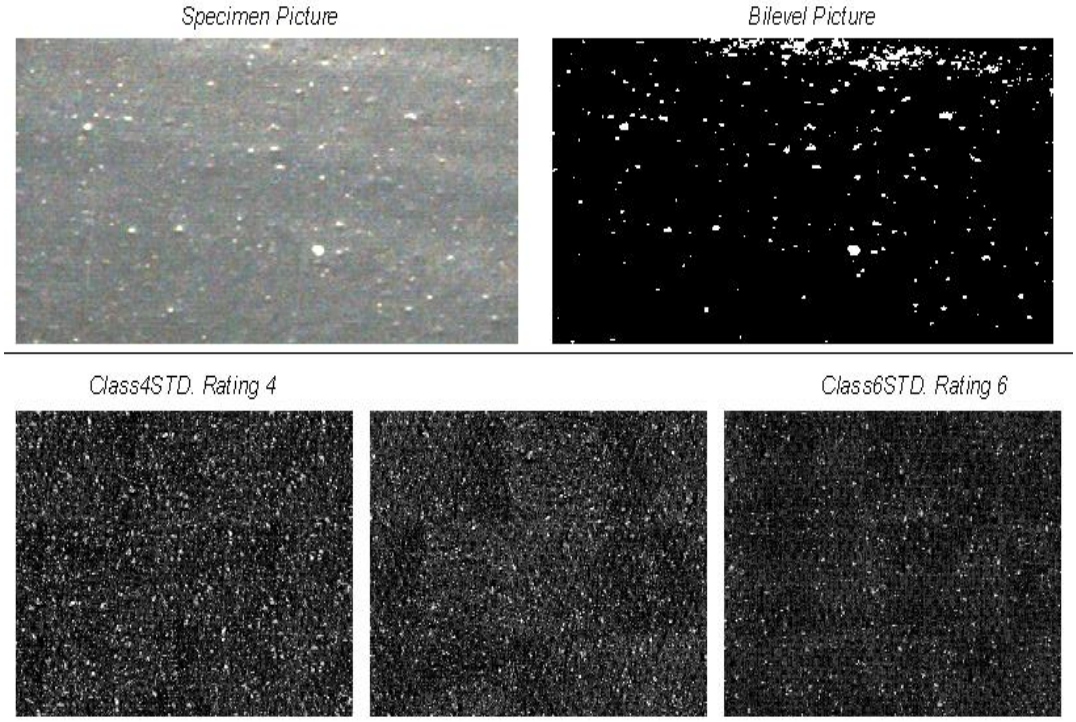


Figure 4.18: Carbon black dispersion for control sample.

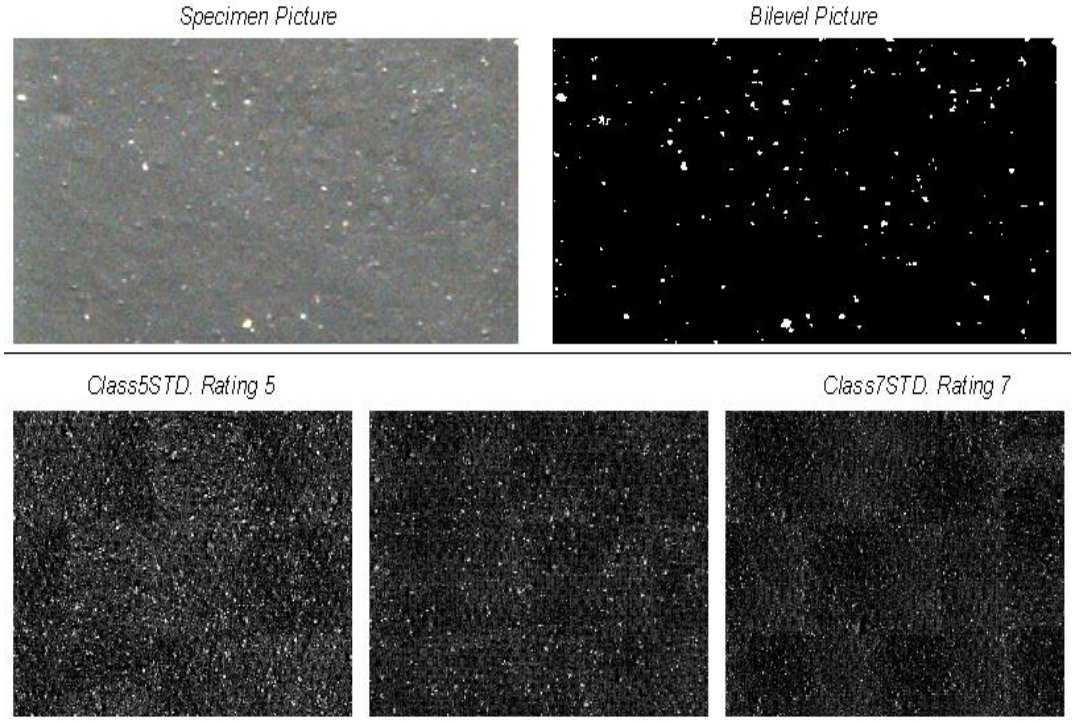


Figure 4.19: Carbon black dispersion for zinc fatty soap sample.

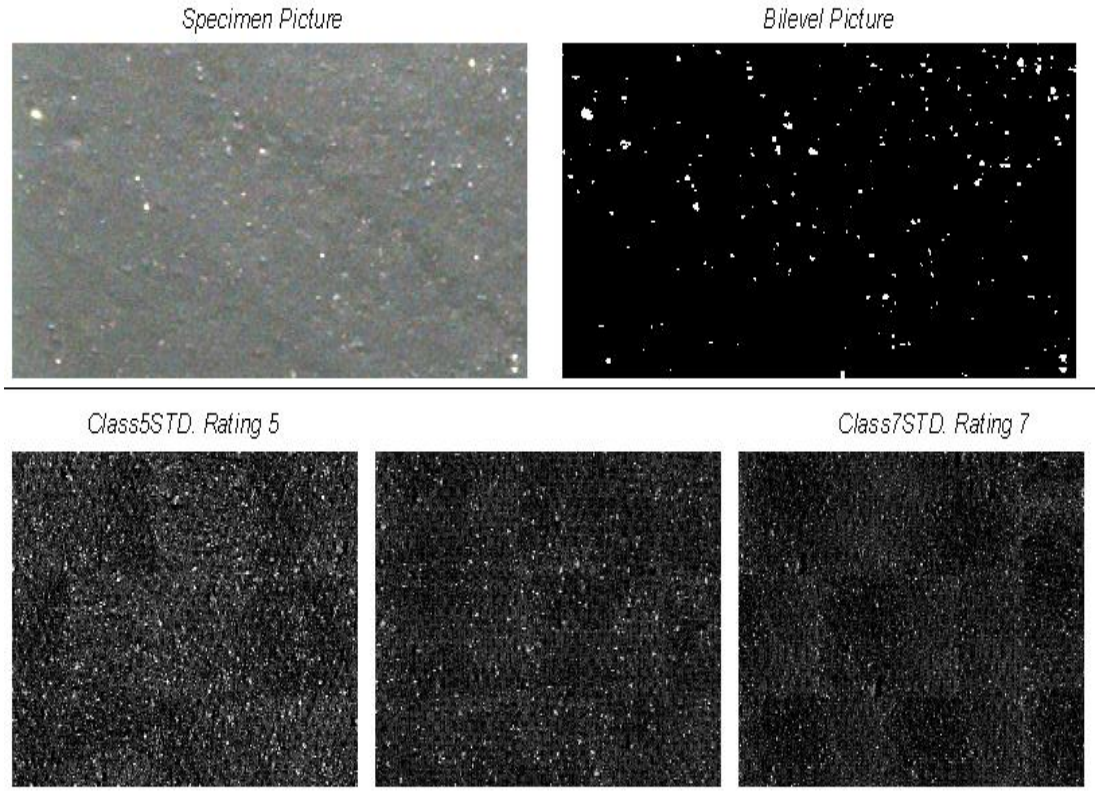


Figure 4.20: Carbon black dispersion for zinc stearate.

CHAPTER FOUR

CONCLUSION

The iodine value is 55.12 gI_2/100g. Iodine value is used to estimate the unsaturation of the product. The higher iodine value, means the higher unsaturated fatty acids are attached. The acid number is 158.95 mgKOH/g. It used to quantify the amount of acid present in the sample. The acid value is high and due to unsaturated soap.

There are four high intensity peaks show on the chromatogram. Hexadecanoic acid, Octadecanoic acid and Tetradecanoic acid are saturated fatty acids. The unsaturated fatty acid shows on the chromatogram, which is trans - 9 Octadecanoic acid. The unsaturated fatty acid can reduce the blooming effects on the compounder. A double bond of fatty acids, zinc soaps of branched or aromatic carboxylic acids are soluble in rubber. They provide substantial improvement in creep and modulus reproducibility. Both derivatization methods show same chromatogram distribution. The price of BF3-methanol is cheaper than silylation reagent. The BF_3-methonol method will be used in future study.

The melting point of the synthesis sample is much lower than the zinc stearate which is normally in range of 120-130 ℃. The melting point for the synthesis sample is 100.1 ℃. The presence of unsaturation (double bonds) in soap tend to lower the melting point of these compound. The double bonds lower the melting point of a fatty acid chain, is that the sections of the chain attached to the double bond are attached cis-wise to each other.

The synthesis soap also effectively improve the flow ability of the compounder. It starts to be effective in the lower temperature range of compounding and can be used for mastication in a separate stage as well as for single stage mixing. The zinc fatty acids soap has no improvement tensile effect and hardness to the rubber compounds. The zinc soaps slightly improve carbon black dispersion compared with the control sample.

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